

**PILOT PLANT EVALUATION  
OF  
THE EFFECTIVENESS OF  
UV/OZONE OXIDATION  
FOR  
THE REMOVAL OF  
VOLATILE ORGANIC CHEMICALS**

**REPORT TO  
THE CITY OF PASADENA**

**MARCH, 1988**



*R*

**JAMES M. MONTGOMERY, CONSULTING ENGINEERS, INC.**

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000838

March 9, 1988

Mr. Thomas K. Underbrink  
Water Engineering Manager  
City of Pasadena  
Water and Power Department  
150 South Los Robles Avenue, Suite 200  
Pasadena, CA 91101

Dear Mr. Underbrink:

In accordance with our amended contract (Contract Amendment No. 12,978) dated December 23, 1986, James M. Montgomery Consulting Engineers, Inc. (JMM) is pleased to submit this final report entitled "Pilot Plant Evaluation of the Effectiveness of UV/Ozone Oxidation for the Removal of Organic Chemicals." This report summarizes the results of the pilot study which evaluated the overall effectiveness of two commercially available UV/Ozone oxidation systems in removing trichloroethylene (TCE), tetrachloroethylene (PCE), and carbon tetrachloride (CTC) from contaminated Pasadena groundwater. Aside from the UV/ozone tests, a few "special" studies were performed to provide a cursory evaluation of the comparative effectiveness of two alternative advanced oxidation processes (AOP): ozone/peroxide and UV/ozone/peroxide.

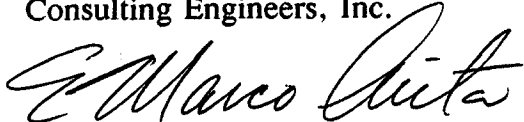
Results of this study indicated, when treating for volatile organic chemicals (VOCs) in the liquid-phase (i.e., contaminated well water), that the UV/ozone oxidation process was effective at destroying TCE and PCE but was not effective at destroying CTC. As a result, a new treatment alternative which couples air stripping with an AOP air pollution control system is proposed. Oxidation of VOCs in the gas-phase, as opposed to the liquid-phase, theoretically should be more efficient.

Finally, using the pilot study results, revised capital and O&M cost estimates for UV/ozone treatment (achieving 99%, 95%, and approximately 50% removals of TCE, PCE, and CTC, respectively) were prepared. The preliminary UV/ozone cost estimates were determined prior to the pilot study and were reported in the previously submitted Treatability/Feasibility report. In addition, the revised UV/ozone estimates are compared with cost estimates for other treatment alternatives deemed viable.

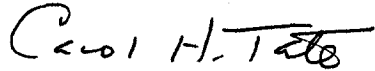
It has been a great pleasure working with you and the other participants during this pilot study. We look forward to continuing to work with you during the next phase of our contract.

Respectfully yours,

JAMES M. MONTGOMERY  
Consulting Engineers, Inc.



E. Marco Aieta, Ph.D.  
Manager of Applied Research Department



Carol H. Tate, D.Env.  
Vice President

/iew

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## EXECUTIVE SUMMARY

## **EXECUTIVE SUMMARY**

### **CONTRACT OBJECTIVES**

The City of Pasadena retained JMM to perform a pilot study to evaluate (1) the overall effectiveness of the UV/Ozone oxidation process in removing trichloroethylene (TCE), tetrachloroethylene (PCE), and carbon tetrachloride (CTC) from its contaminated drinking-water supply wells, and (2) the specific effectiveness of two commercially available UV/Ozone treatment systems. Specific objectives outlined by the contract were:

- o Verify that the UV/Ozone process would effectively remove VOCs from Pasadena's groundwater;
- o Refine capital and operation & maintenance (O&M) cost estimating data for the two commercially available UV/Ozone systems;
- o Determine design criteria for the UV/Ozone process; and
- o Investigate a service-provider concept for UV/Ozone treatment of Pasadena's groundwater, if the treatment process proved effective for VOC removal.

The two UV/Ozone equipment manufacturers selected for evaluation were ULTROX International (ULTROX) and Water Management, Inc. (WMI).

### **CURRENT VOC LEVELS AT WELL #25**

As part of the pilot investigation, water samples were collected twice (in mid-October) from Well #25 and analyzed for TCE, PCE, and CTC. The average concentrations measured were:

TCE	-	18 $\mu$ g/L
PCE	-	4 $\mu$ g/L
CTC	-	21 $\mu$ g/L

The earlier Hydrogeologic Investigation Report projected the maximum TCE concentration (at Well #25) to reach 170  $\mu\text{g/L}$  in the next 20- to 30-years and remain detectable for 40 years after the peak. Historical data from Well #25 indicate a trend of increasing concentration over time, for each of the three VOCs. During the past two to three years, the greatest increase in concentration has been for CTC. The maximum concentrations measured to date are: TCE = 32  $\mu\text{g/L}$ ; PCE = 6.3  $\mu\text{g/L}$ ; CTC = 23  $\mu\text{g/L}$ .

## **TREATED WATER GOALS**

The current State of California action levels for TCE, CTC, and PCE are 5-, 5-, and 4- $\mu\text{g/L}$ , respectively. These State regulations for TCE and CTC are the same as the national primary drinking water regulations, promulgated by the USEPA in July, 1987 (Federal Register, July 8, 1987). The USEPA's final regulation for PCE is scheduled for promulgation by June, 1988.

In light of these regulations, and to allow a margin of safety, the treated water goals were set at 2  $\mu\text{g/L}$  for each VOC. The approximate maximum concentrations tested in this pilot study were 200  $\mu\text{g/L}$  for TCE and CTC, and 20  $\mu\text{g/L}$  for PCE. Thus, translating the treated water goal into terms of percent removal, the treatment goals were 99% removal of TCE and CTC, and 90% removal of PCE.

## **VOC REMOVAL EFFICIENCIES USING UV/OZONE**

The ULTROX and WMI UV/Ozone treatment systems were subjected to extensive testing to determine the effectiveness of each system in removing TCE, PCE, and CTC from drinking water when initial VOC concentrations ranged from 2- to 200- $\mu\text{g/L}$ . The drinking water used for these tests was uncontaminated water from Windsor Reservoir which had been spiked with VOCs just before going through the UV/ozone systems. A limited number of experiments were performed with water from Well #25. The results were similar for both water supplies. The best removals demonstrated by each system, in comparison with the treatment goals, were:

Demonstrated RemovalsTreatment Goals

## WMI:

TCE = 50% removal	99% removal
PCE = 50% removal	90% removal
CTC = 15% removal	99% removal

## ULTROX:

TCE = 99% removal	99% removal
PCE = 99% removal	90% removal
CTC = 80% removal	99% removal

Thus, the WMI system was not able to demonstrate satisfactory removals (in relation to the treatment goals) for any of the VOCs tested; the ULTROX system demonstrated excellent TCE and PCE removals, but unsatisfactory removal of CTC.

**SPECIAL STUDY USING H<sub>2</sub>O<sub>2</sub>/OZONE OXIDATION**

As a result of some very recent and successful studies using the H<sub>2</sub>O<sub>2</sub>/Ozone Advanced Oxidation Process (AOP) for VOC removal, a special study was performed to evaluate the effectiveness of H<sub>2</sub>O<sub>2</sub>/Ozone oxidation in comparison with UV/Ozone oxidation. Results of this limited testing indicated that H<sub>2</sub>O<sub>2</sub>/Ozone oxidation can provide a degree of treatment comparable to UV/Ozone oxidation, but requires a much lower ozone dose and shorter contact time. The actual removals attained were:

<u>VOC</u>	<u>Initial Concentration</u>	<u>Percent Removal</u>
TCE	≅ 200 µg/L	> 99%
PCE	≅ 1 µg/L	79%
CTC	≅ 200 µg/L	67%

## ALTERNATIVE TREATMENT SCENARIOS

As a result of the poor CTC removal efficiencies demonstrated by UV/Ozone treatment, several new (i.e., not considered in the Treatability/Feasibility Report) alternative treatment scenarios were assessed. These alternative treatment scenarios were:

- o Liquid-phase AOP with liquid-phase granular activated carbon (GAC);
- o Liquid-phase  $\text{H}_2\text{O}_2$ /Ozone with air stripping (AS) plus GAC air pollution control (GAC-APC); and
- o Air stripping with AOP air pollution control (AOP-APC).  
(Liquid-phase  $\text{H}_2\text{O}_2/\text{O}_3$  prior to air stripping with AOP-APC is another option.)

These treatment alternatives were evaluated in regard to associated advantages, disadvantages, and costs for full-scale implementation.

## COSTS

The revised cost for UV/Ozone treatment (ULTROX only), the cost for  $\text{H}_2\text{O}_2$ /Ozone treatment, and the costs associated with the newly considered treatment alternatives listed in the previous paragraph, were estimated and compared with the cost estimates presented in the Treatability/Feasibility Report. These estimates are summarized in Table E1, along with a qualitative assessment as to whether or not the treatment alternative is viable. The viable alternatives listed in order of increasing costs are:

- o AS + AOP-APC
- o AS + GAC-APC
- o  $\text{H}_2\text{O}_2$ /Ozone + AS + GAC-APC
- o  $\text{H}_2\text{O}_2$ /Ozone + liquid-phase GAC
- o GAC alone

The first alternative (AS + AOP-APC) is known to be effective in destroying TCE and PCE, but has never been tested for CTC removal.

**TABLE E1**  
**COMPARISON OF ESTIMATED TREATMENT COSTS FOR**  
**ALL ALTERNATIVE TREATMENT PROCESSES CONSIDERED**

Treatment Alternative	Viable Alternative	Reason If Not Viable	Total Capital Cost (\$)	Annual O&M Cost (\$/Yr)	Total Annual Cost (\$/Yr)	Unit Cost (\$/AF)
Air Stripping	No	AQMD will not approve the use of this process without APC if > 1lb/day of VOCs are discharged. (Regulations pending.)	\$ 550,000	\$ 44,000	\$ 100,000	22
H <sub>2</sub> O <sub>2</sub> /Ozone	No	Does not effectively remove CTC.	387,000	81,000	121,000	27
Air Stripping plus AOP Air Pollution Control	Yes (?)	This is a new technology; not sure if it will effectively remove CTC.	1,890,000	130,000	323,000	72
Air Stripping and GAC Air Pollution Control	Yes		1,200,000	340,000	460,000	104
H <sub>2</sub> O <sub>2</sub> /Ozone plus Air Stripping plus GAC Air Pollution Control	Yes		1,600,000	300,000	470,000	105
H <sub>2</sub> O <sub>2</sub> /Ozone plus GAC	Yes		2,300,000	300,000	540,000	120
Granular Activated Carbon (GAC)	Yes		1,950,000	380,000	580,000	130
UV/Ozone (Ultrax, revised)	No	Does not effectively remove CTC.	3,822,000	581,000 (462,000)	970,000 (851,000)	216 (190)

\* The numbers in parentheses were based on an ozone power consumption of 10 KWH/lb O<sub>3</sub> which is the industrial average. The other numbers were based on a power consumption of 18.8 KWH/ lb O<sub>3</sub>, determined during the pilot study.

Of these viable treatment alternatives, their estimated costs increase in the following order:

	<u>Capital Cost (\$)</u>	<u>Unit Cost (\$/AF)</u>	<u>Accuracy of Cost Estimates</u>
AS + AOP-APC	1,890,000	72	-40% / +140%
AS + GAC-APC	1,200,000	104	-30% / +50%
H <sub>2</sub> O <sub>2</sub> /Ozone + AS + GAC-APC	1,600,000	105	-30% / +60%
H <sub>2</sub> O <sub>2</sub> /Ozone + liquid-phase GAC	2,300,000	120	-30% / +60%
GAC alone	1,950,000	130	-30% / +50%

## TREATMENT OPTIONS

After assessing the advantages, disadvantages and cost of each of these processes in comparison with the advantages, disadvantages and costs of those processes included in the Treatability/Feasibility Report, the four most promising treatment options available to the City of Pasadena are:

1. Proceed with the design of liquid-phase GAC treatment. This is a proven technology for TCE, PCE and CTC removal and could be designed and constructed without further testing. The major drawback to this option is its high cost.
2. Design and construct an air stripping tower that includes a GAC-APC system. The main advantages of this option are the decreased cost compared to liquid-phase GAC. The disadvantages are those associated with air stripping towers, aesthetic appearance and noise.
3. Perform a thorough pilot-scale evaluation of the air stripping plus AOP-APC treatment system (as outlined in Section 7) prior to deciding which of the viable treatment alternatives would provide the best full-scale treatment. A more complete evaluation of the AS + AOP-APC treatment process (i.e., the inclusion of H<sub>2</sub>O<sub>2</sub>/ozone oxidation in the stripping tower) is possible under this option. Other advantages include the potential for elimination of ultimate disposal problems, and the lower cost of AOP-APC treatment compared with systems involving GAC. The main disadvantage is the time delay imposed by the pilot study on the design for full-scale treatment system. This delay could result in



spreading of the contaminated water plume to other wells, which would mean further costs to purchase replacement water or treatment systems.

4. Begin the thorough pilot-scale study of the air stripping plus AOP-APC treatment system, and simultaneously, design the full-scale air stripping portion of the treatment facility. The decision to design for full-scale AOP emissions control, or full-scale GAC emissions control, could be made near the end of the extended pilot study. This will minimize the time delay in construction of a full-scale treatment system, since the air stripper is a common element to both emissions control options. Minimizing this time delay would prevent further problems and costs associated with the spread of the contaminated plume to other wells.

JMM recommends that option 4 be selected since it is the most environmentally sound and economical of the viable alternatives, which will accomplish the treatment objectives in a timely fashion. This option will allow for the most cost effective air stripper with emissions control system with the minimum time delay. Under option 4, a complete treatment system utilizing either GAC or AOP for emissions control, would be completed and operational within 23 months.

**SECTION 1**

## **SECTION 1**

### **INTRODUCTION**

#### **BACKGROUND**

In January, 1980, several wells within the Raymond Basin were found contaminated with volatile organic chemicals (VOCs)--specifically, trichloroethylene (TCE) and carbon tetrachloride (CTC). The City of Pasadena's (City) Well #25 was among those found contaminated. By 1982, the VOC plume was observed to be spreading towards the City's Well #52. Preliminary investigations suggested Jet Propulsion Laboratory (JPL) as a likely source.

In January, 1986, James M. Montgomery, Consulting Engineers, Inc. (JMM) was contracted by the City of Pasadena, with the Jet Propulsion Laboratory and the Lincoln Avenue Water Company joining in support, to perform a complete hydrogeologic investigation of the possible sources of VOC contamination and feasibility of several treatment alternatives. The hydrogeologic investigation was completed in July, 1986 and in November, 1986 the treatability/feasibility study was completed. The treatability/feasibility study evaluated the cost, effectiveness, reliability, and advantages/disadvantages of three innovative treatment technologies--air stripping in conjunction with granular activated carbon (GAC) air pollution controls (AS + GAC-APC), granular activated carbon (GAC) adsorption, and UV/ozone oxidation--which could be used to remove the VOCs from the contaminated well water. Based on the information presented in the treatability/feasibility report (JMM, November, 1986), UV/ozone oxidation was selected as the most promising treatment alternative and JMM was retained by the City to perform a pilot-scale evaluation of the two commercially available UV/ozone systems. This report presents and discusses the findings of this pilot study.

#### **REVIEW OF MEASURED AND PROJECTED VOC CONCENTRATIONS**

Beginning in 1980, the City of Pasadena Wells #25 and #52 were sampled and tested for VOC contamination. Based on this testing, TCE, CTC and tetrachloroethylene (PCE) appeared to be the contaminants of primary concern and their concentrations appeared to be gradually increasing. The trends in TCE, PCE, and CTC concentrations at these

wells, using data collected between 1980 and 1985, was discussed in the hydrogeologic report (included in the Appendices of the Treatability/Feasibility Report) and are presented here in Figures 1a, 1b, and 1c (Well #25) and Figures 2a and 2b (Well #52). Water samples were collected recently (October, 1987) from Well #25, as part of this pilot investigation, and analyzed for TCE, PCE, and CTC. (Both of these wells are currently shut down, and thus, not routinely monitored.) The concentrations measured were:

<u>Sampling Date</u>	<u>TCE (<math>\mu\text{g/L}</math>)</u>	<u>PCE (<math>\mu\text{g/L}</math>)</u>	<u>CTC (<math>\mu\text{g/L}</math>)</u>
10/13/87	17	6.3	18
10/14/87	18	1.3	23

According to the data for Well #25, the average VOC concentrations measured in 1985 (the last year of regular sampling) were:

<u>Sampling Date</u>	<u>TCE (<math>\mu\text{g/L}</math>)</u>	<u>PCE (<math>\mu\text{g/L}</math>)</u>	<u>CTC (<math>\mu\text{g/L}</math>)</u>
1985 avg	12	0.9	10

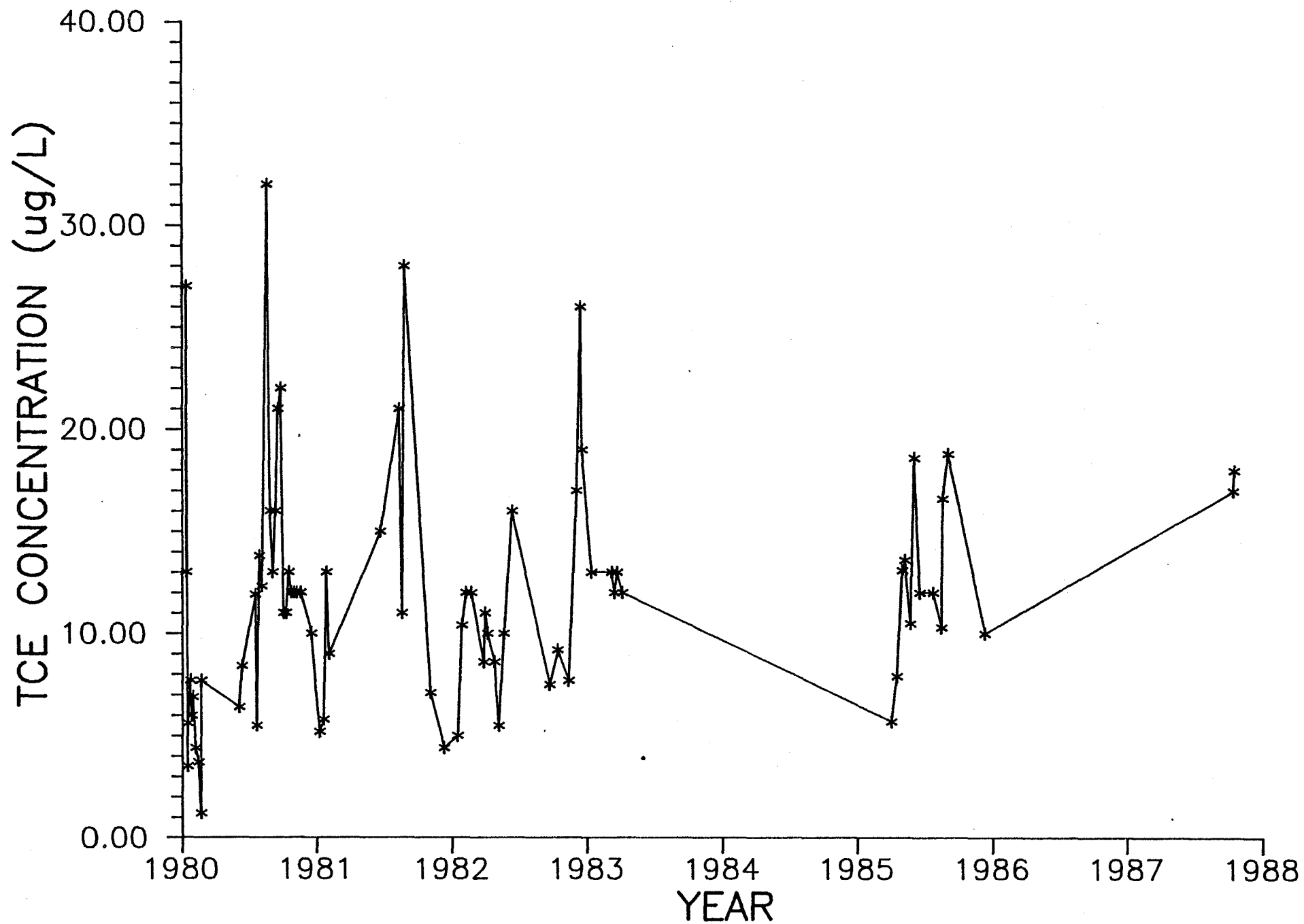
Comparison of these 1985 average concentrations with the 1987 measurements indicate that concentrations of all three VOCs are continuing to increase, with the apparent greatest increase being for CTC. As was discussed in the hydrogeologic report, the maximum TCE concentration at Well #25 is expected to reach a peak of  $170 \mu\text{g/L}$  in the next 20- to 30-years and remain detectable for approximately 40-years after the peak.

Two other VOC's were detected in the contaminated wells. Chloroform ranging in concentrations between  $1.0$  and  $6.5 \mu\text{g/L}$ , was found on two occasions in each of the contaminated wells #25 and #52. 1,2-dichloroethane was seen once in well #25.

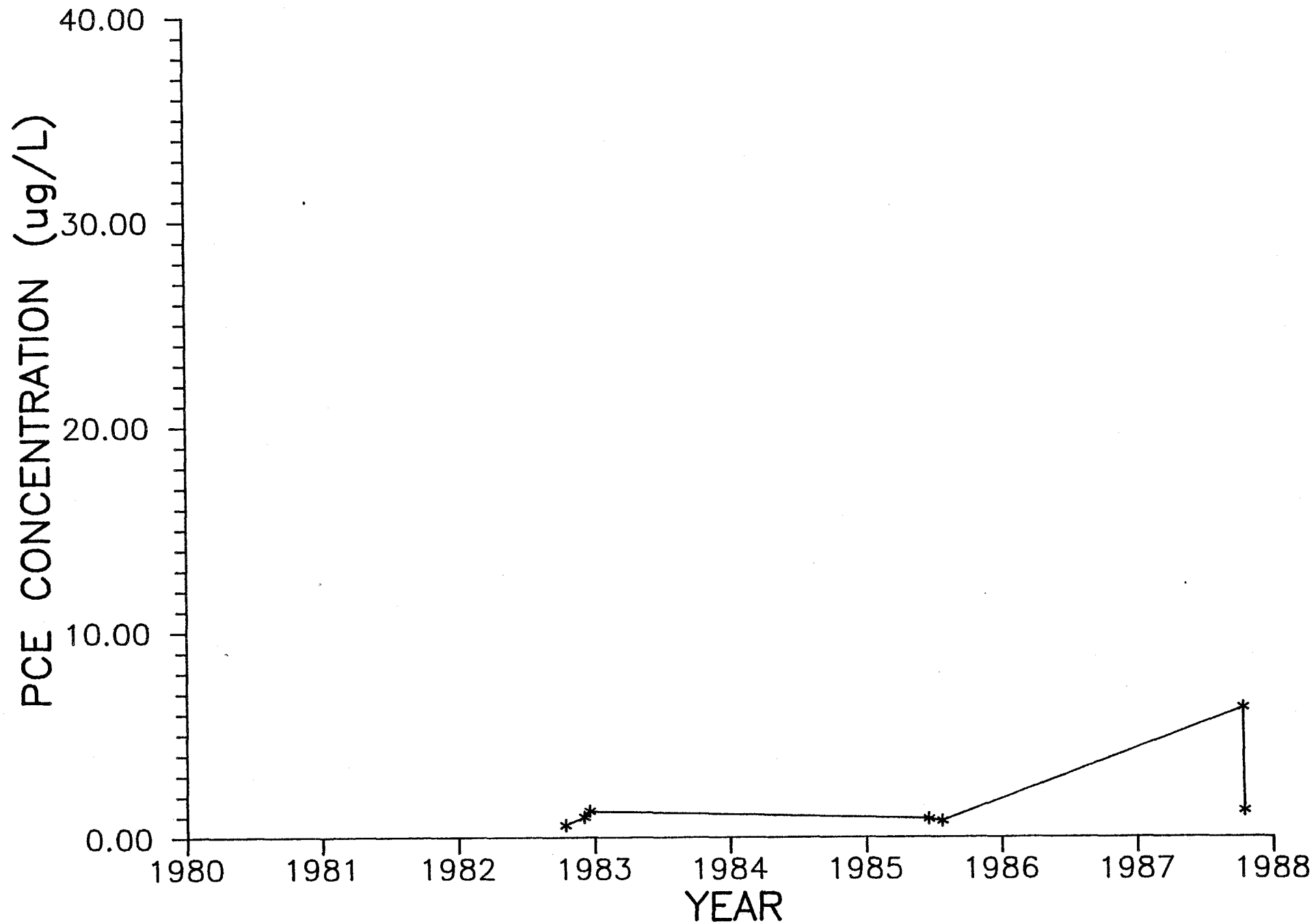
## **FINDINGS OF THE TREATABILITY/FEASIBILITY STUDY**

Several treatment alternatives were considered during the treatability/feasibility evaluation:

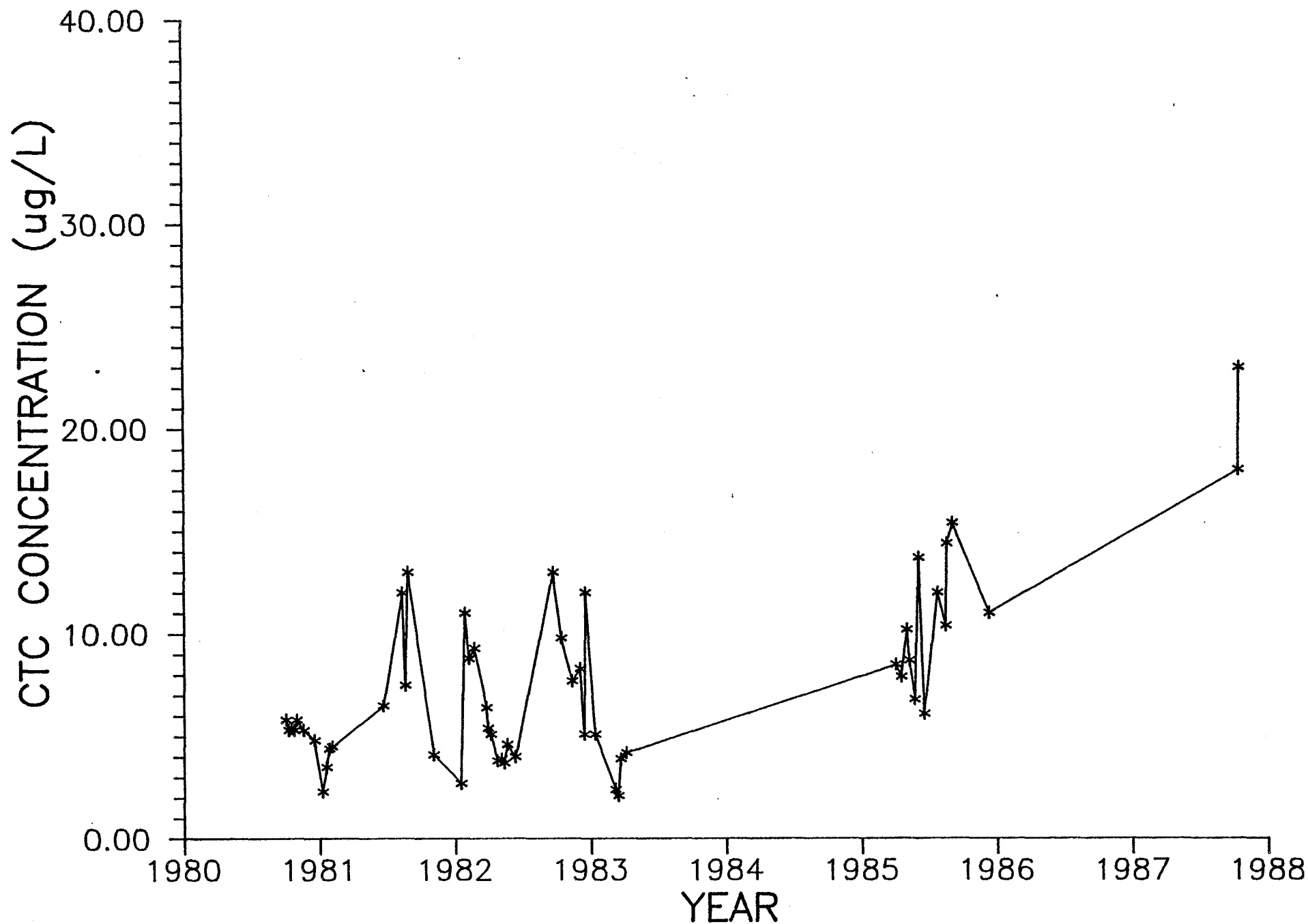
- o Installation of new wells (in an uncontaminated area) rather than treatment of the contaminated wells;



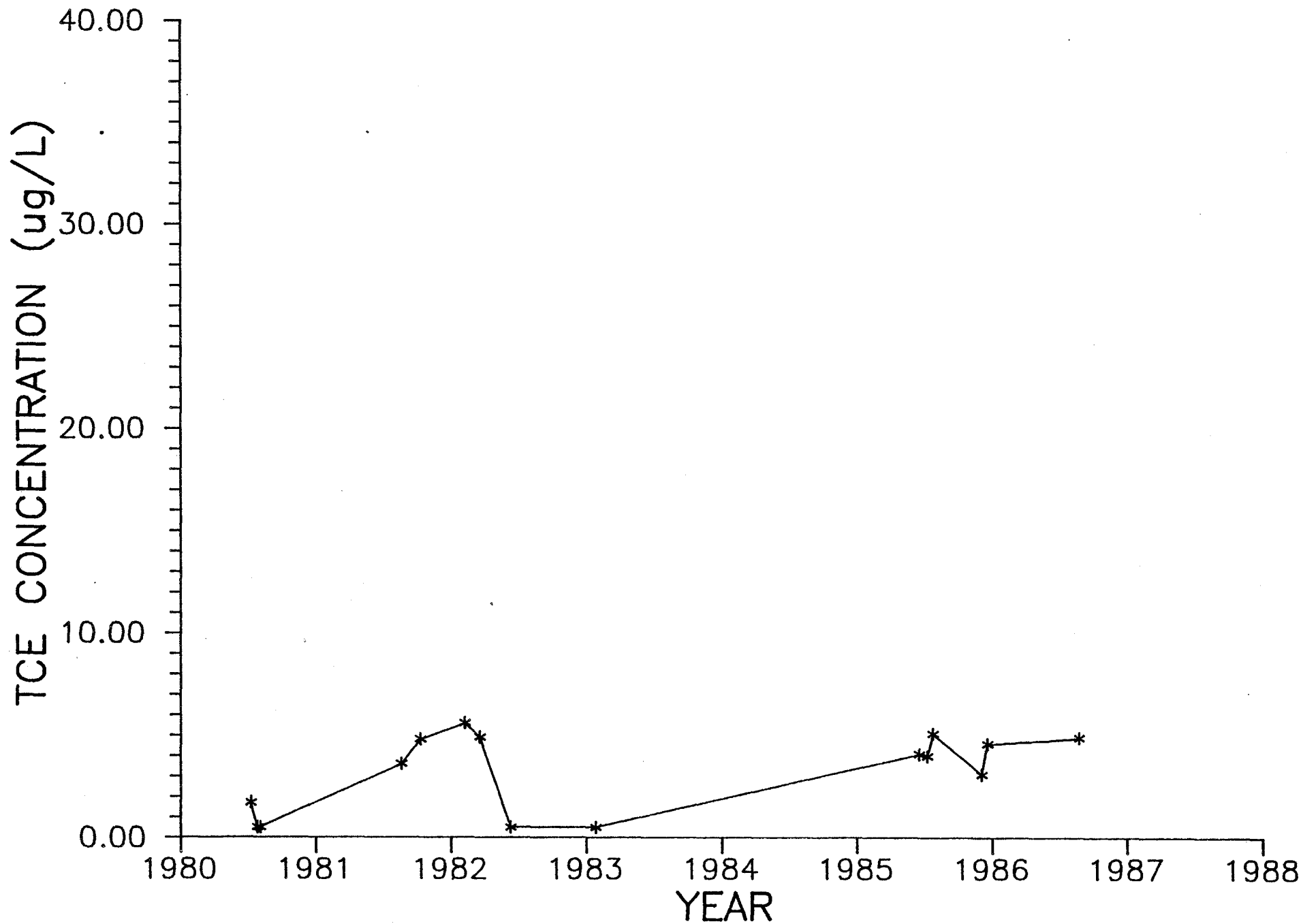
HISTORICAL TCE CONCENTRATIONS AT WELL #25  
FIGURE 1A



HISTORICAL PCE CONCENTRATIONS AT WELL #25  
FIGURE 1B

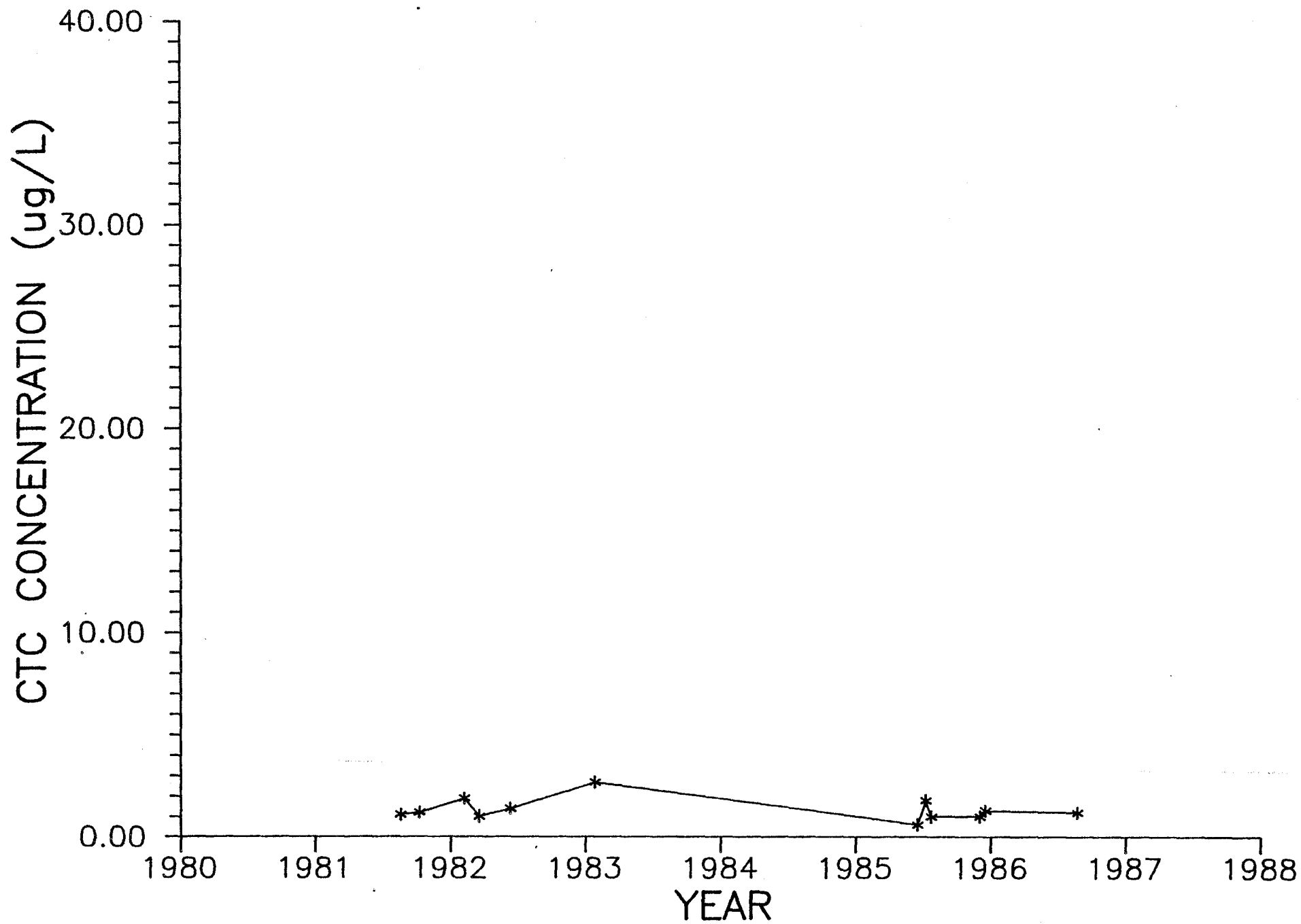


HISTORICAL CTC CONCENTRATIONS AT WELL #25  
FIGURE 1C



HISTORICAL TCE CONCENTRATIONS AT WELL #52  
FIGURE 2A





HISTORICAL CTC CONCENTRATIONS AT WELL #52  
FIGURE 2B

- o Blending of contaminated with uncontaminated well water;
- o Air stripping (AS);
- o Air stripping in conjunction with a granular activated carbon air pollution control (GAC-APC) system;
- o UV/ozone oxidation; and
- o Granular activated carbon (GAC) adsorption.

The no treatment, blending, and air stripping alternatives were eliminated early in the study for various reasons, with the fundamental objection being poor public perception. The remaining alternatives were evaluated from the standpoint of effectiveness, reliability, advantages/disadvantages and cost. A summary of the estimated cost of each alternative is shown below. (These estimates are for the treatment of Wells #25 and #52 only; they do not include the cost of treating additional water for Lincoln Avenue Water Company, as was discussed in the treatability/feasibility report.) As explained in the treatability/feasibility report, when preparing these estimates, the O&M and capital costs (where applicable) were staged in conjunction with projected changing VOC concentrations, over the expected life of the contaminant plume.

<u>Treatment Process</u>	<u>Capital (\$)</u>	<u>O&amp;M (\$/yr)</u>	<u>Unit Cost (\$/AF)</u>
UV/Ozone (WMI)	2,930,000	134,000	85
Air stripping + GAC-APC	1,200,000	340,000	104
Granular Activated Carbon	1,950,000	380,000	130
UV/Ozone (ULTROX, original estimate)	2,920,000	267,000	126

After carefully reviewing the treatability/feasibility report, the City elected to pilot the UV/ozone process because it appeared to provide the most effective, environmentally sound, and cost effective treatment solution. The two UV/ozone system manufacturers selected to participate in this pilot study were Ultrox International (ULTROX) and Water Management, Inc. (WMI). The pilot testing phase of this study has been completed

(mid-November, 1987) and the results are presented in this report.

## **UV/OZONE PILOT STUDY OBJECTIVES**

The overall objectives for this pilot-scale evaluation were to:

- o Verify that the UV/Ozone process would effectively remove VOCs from Pasadena groundwater;
- o Refine capital and operation & maintenance (O&M) cost estimating data; and
- o Determine design criteria.

The ultimate treated water goal was set at 2  $\mu\text{g/L}$  for each of the three VOCs. The approximate maximum concentrations tested in this pilot study were 200  $\mu\text{g/L}$  for TCE and CTC, and 20  $\mu\text{g/L}$  for PCE. Translated into terms of percent removal, the treated water goals were 99% removal of TCE and CTC, and 90% removal of PCE. This treatment goal was based on the current state and federal drinking water regulations, plus a margin of safety. The current State of California action levels for TCE, CTC, and PCE are 5-, 5-, and 4- $\mu\text{g/L}$ , respectively. These state regulations for TCE and CTC are the same as the national primary drinking water regulations, which were promulgated by the USEPA in July, 1987 (Federal Register, July 8, 1987). The USEPA's final regulation for PCE is scheduled for promulgation before June, 1988.

The scope of work for this study was divided into two phases: Phase I - Intensive Monitoring and Phase II - Long-Term Monitoring.

### **Phase I - Intensive Monitoring**

Specific objectives for the intensive monitoring phase were to:

- o Test the effectiveness of each vendor's system in reducing a range of TCE, PCE, and CTC concentrations to the treated water goal of 2  $\mu\text{g/L}$  or less;
- o Optimize the operation of each system with respect to (1) UV dose, (2) ozone dose, (3) contact time;

- o Ensure that little or no VOCs were being stripped and vented directly to the atmosphere (WMI only); and
- o Verify that harmful oxidation by-products were not being generated, in either the water or exhaust gas, as a result of the UV/ozone oxidation process.

The third objective, regarding the venting of VOCs, is applicable to WMI's system only; ULTROX's equipment employed a recirculating air system which meant that no gases were vented to the atmosphere.

### **Phase II - Long-Term Monitoring**

The long-term monitoring phase was designed to identify O&M requirements and refine the O&M cost estimates for each system. During this phase of testing, the equipment was to operate continually for a period of two months. As will be discussed, actual testing performed under this phase differed somewhat from what was originally envisioned.

## SECTION 2

## **SECTION 2**

### **DESCRIPTION OF DEMONSTRATION SITE AND EQUIPMENT**

#### **SITE LAYOUT AND UV/OZONE SYSTEMS**

Site preparation was carried out by the City of Pasadena under the direction of JMM. The site was located at Windsor Reservoir and water from the reservoir was used for the pilot testing. The two UV/ozone system manufacturers selected to participate in this pilot study were ULTROX International (ULTROX) and Water Management, Inc. (WMI).

The site layout for the ULTROX UV/ozone system is shown in Figure 3 and is self-explanatory. The initial site layout for the WMI UV/ozone system is depicted in Figure 4a. As will be discussed in more detail under Section 3, the WMI system was modified later in the testing to improve VOC removal efficiencies. The modified system is shown in Figure 4b.

#### **VOC SPIKING SYSTEM**

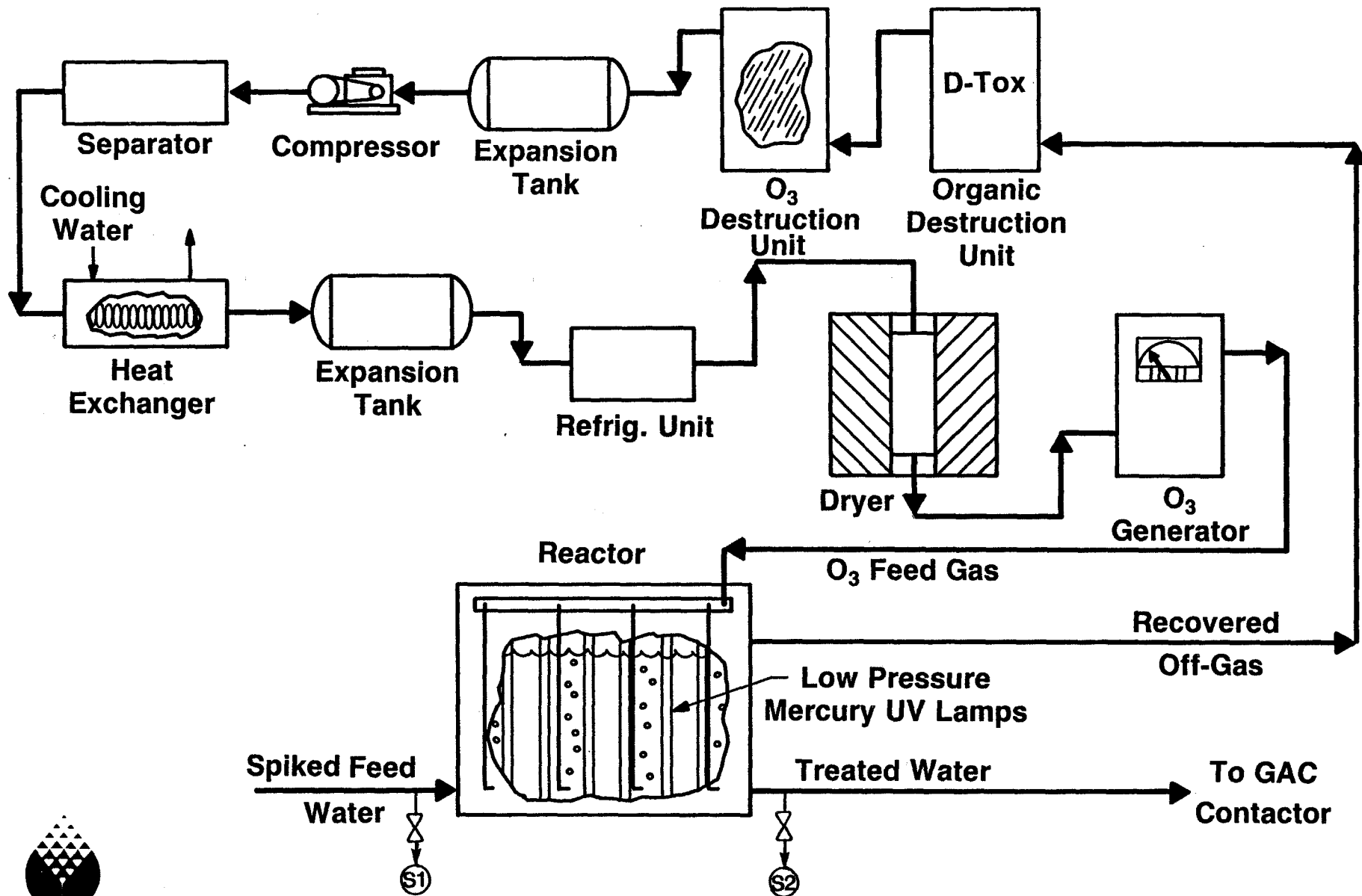
VOCs were spiked into the influent line as shown in Figure 5. Water from Windsor Reservoir was used for the major part of the study. Later, several tests were performed with water from Pasadena Well #25, to determine whether any differences in general water quality between the two water sources, would affect the VOC removal efficiencies of the UV/Ozone treatment.

#### **CARBON ADSORPTION SYSTEM**

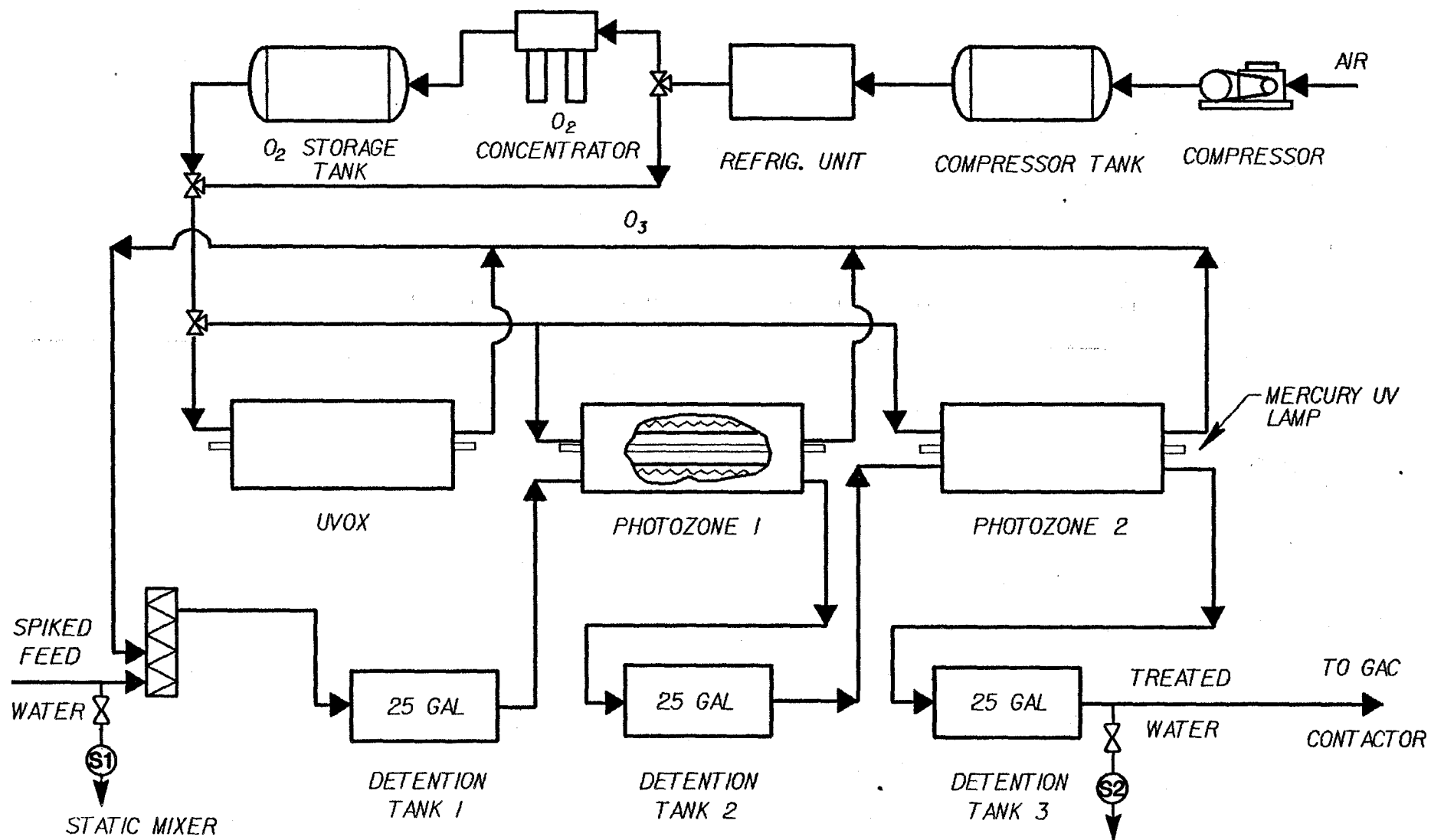
After UV/ozone treatment, the effluent water was passed through a granular activated carbon contactor (Figure 6) to remove any VOCs remaining after treatment, prior to discharge in the Arroyo spreading grounds.

#### **SYSTEM MODIFICATIONS FOR SPECIAL STUDIES**

Towards the end of Phase II, several "special studies" were performed which involved modifications of the WMI system in an effort to improve VOC removals. Another part of the "special studies" evaluated the treatment performance using actual contaminated water from well #25 as compared with treatment performance using water from Windsor

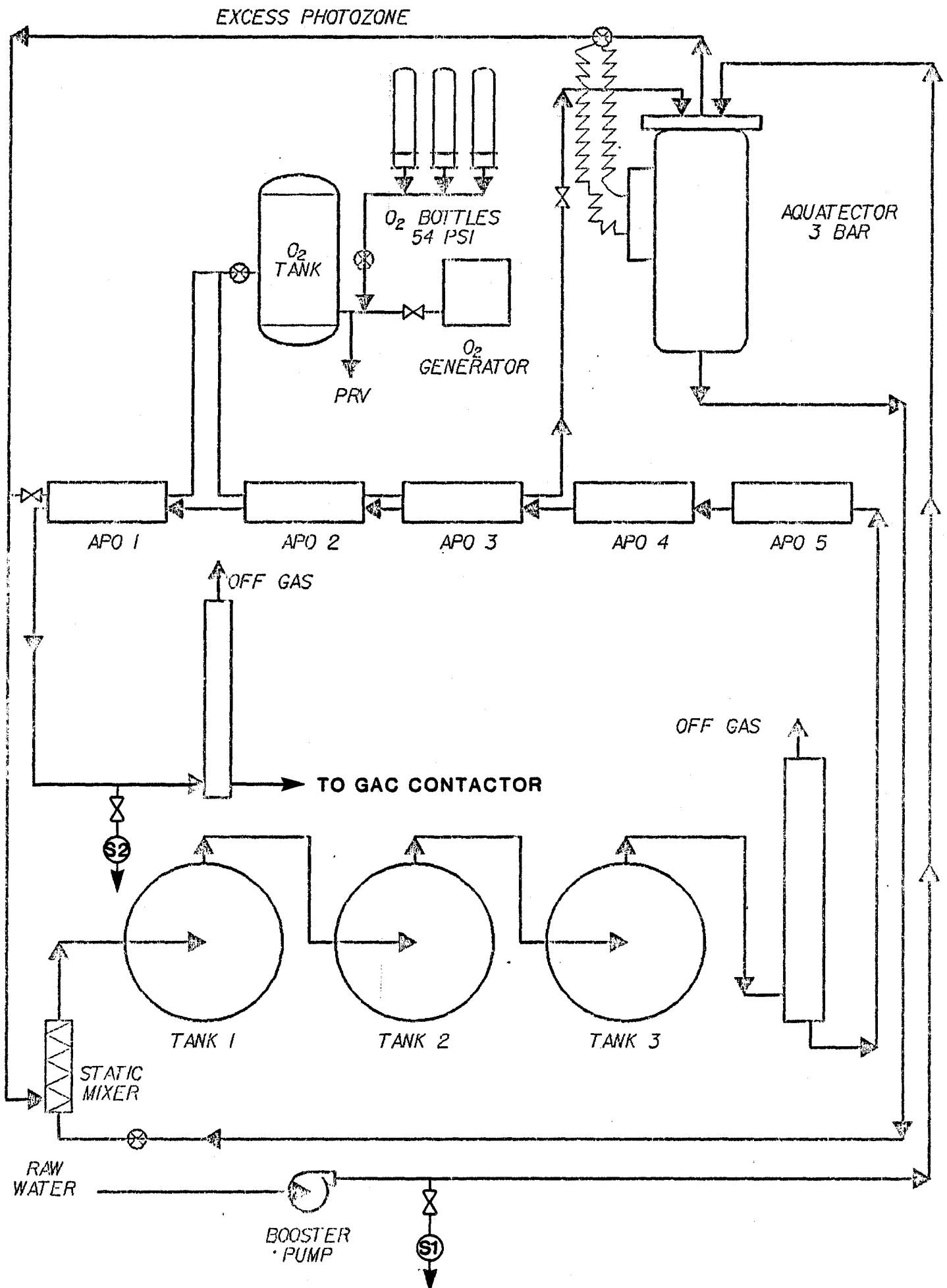


UV/OZONE OXIDATION SYSTEM WITH OFF-GAS RECYCLE  
 SITE LAYOUT AND EXPERIMENTAL SET-UP OF ULTROX UV/OZONE SYSTEM  
 FIGURE 3

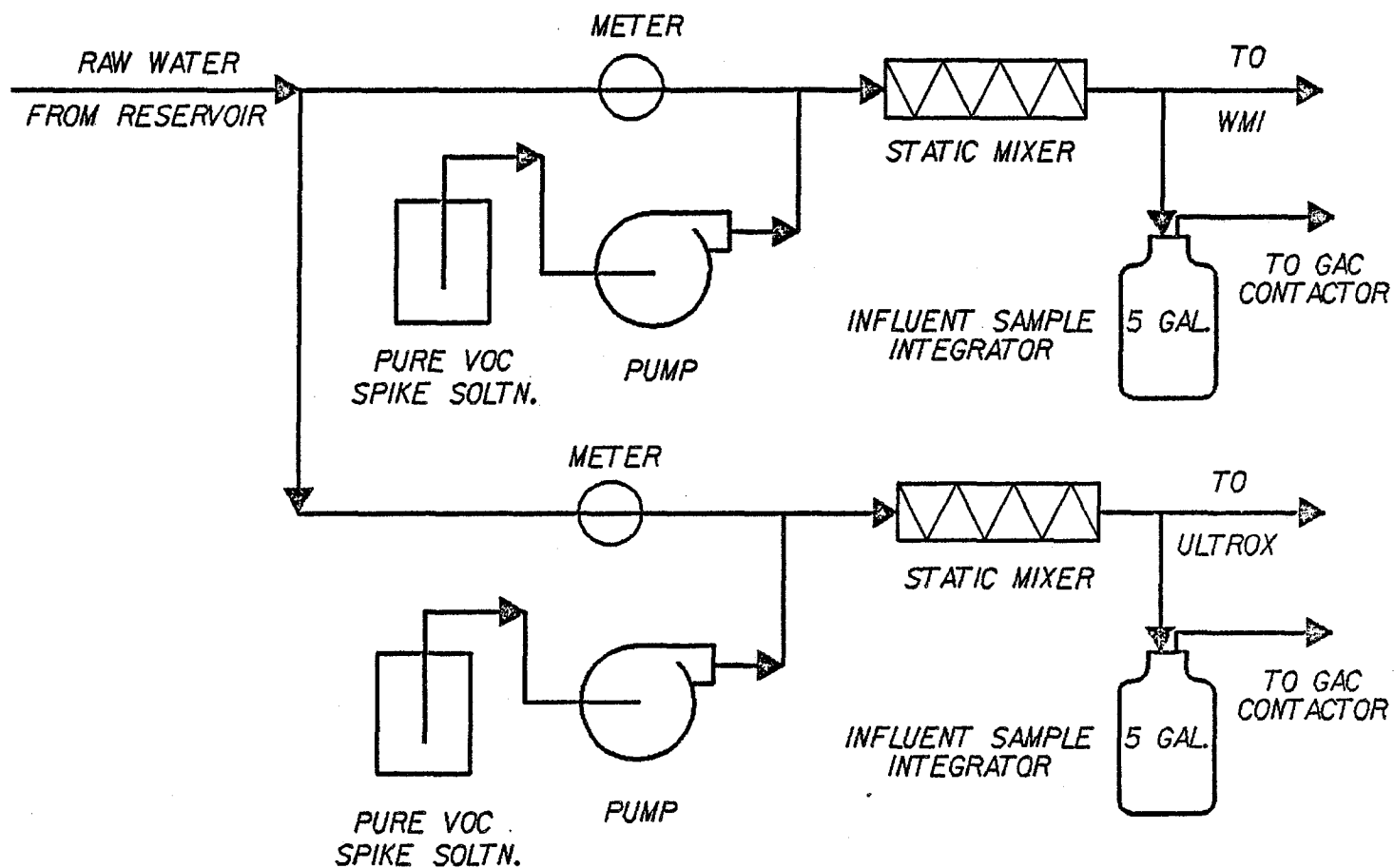


INITIAL SITE LAYOUT AND EXPERIMENTAL SET-UP OF WMI UV/OZONE SYSTEM  
FIGURE 4A

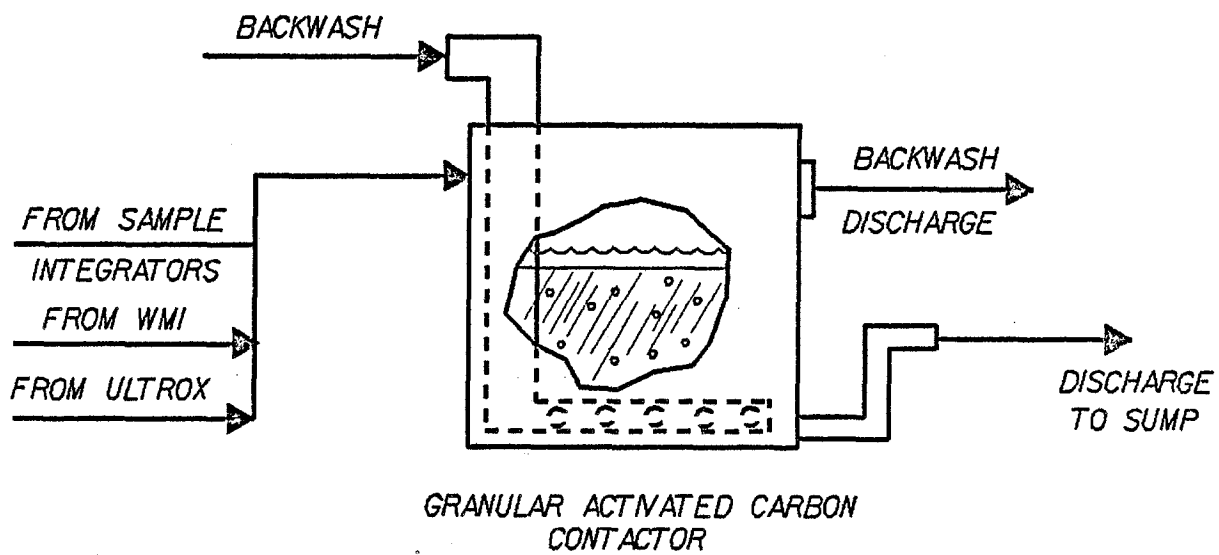




MODIFIED SITE LAYOUT AND EXPERIMENTAL SET-UP OF WMI UV/OZONE SYSTEM  
FIGURE 4B



**VOC FEED SPIKE SYSTEM  
FIGURE 5**



**GRANULAR ACTIVATED CARBON CONTACTOR  
FIGURE 6**

Reservoir. More details are provided in Section 3. In addition, two other advanced oxidation processes,  $\text{H}_2\text{O}_2$ /ozone and  $\text{H}_2\text{O}_2$ /ozone/UV, were studied using the ULTROX system. In these studies,  $\text{H}_2\text{O}_2$  was added after the VOC spike and the static mixer.

**SECTION 3**

## **SECTION 3**

### **EXPERIMENTAL PLAN, SAMPLE COLLECTION AND ANALYTICAL METHODS**

The scope of work for this study was divided into two phases: an intensive monitoring phase (Phase I) and a long-term monitoring phase (Phase II). Phase I ran from the end of June through mid-July and Phase II from the beginning of September through mid-November.

#### **ORIGINALLY PROPOSED DEMONSTRATION WORK**

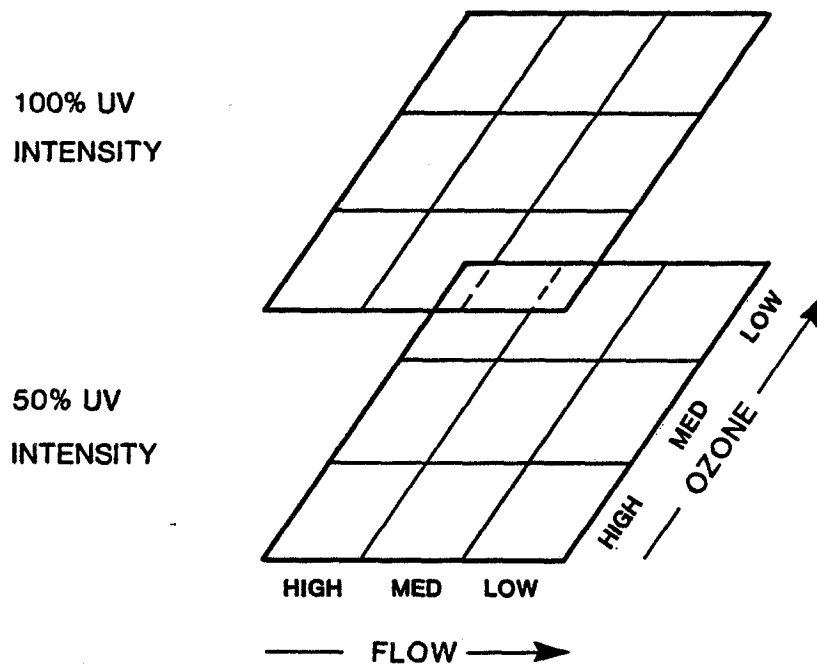
The experimental plan originally proposed for this study was described in detail in the (1) February 2, 1987 JMM Memorandum (from Elaine Wallace), (2) March 31, 1987 JMM Memorandum (from Marco Aieta and Elaine Wallace), and (3) May 29, 1987 letter to Tom Underbrink (from Marco Aieta). The actual experimental plan which was followed was modified somewhat from the proposed plan. The proposed experimental plan, and all modifications from this plan are described briefly in the following paragraphs.

#### **Intensive Phase Testing**

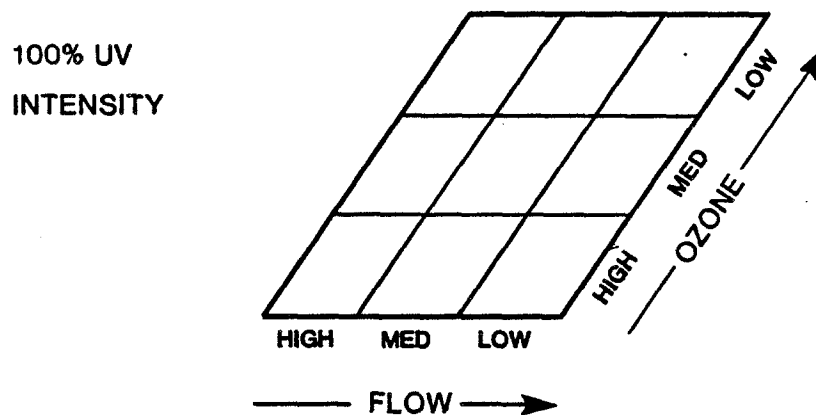
The intensive monitoring phase was designed to evaluate VOC removal efficiencies for several VOC concentrations, water flow rates (or contact times), ozone dosages, and UV dosages. The experimental plan was set up according to the matrix shown in Figure 7 and was applied to both manufacturer's systems. Actual operating conditions, corresponding to the high-, medium-, and low-dosages shown in Figure 7, are provided in Table 1. As a result of delays experienced in getting the equipment set up and operating properly, sufficient time was not available to perform all experiments identified in the sampling matrix and the experimental plan was modified to accommodate as many of the originally proposed tests as possible.

The number of tests completed during the intensive phase are shown in Table 2. For these tests, the equipment was operated for a period of time sufficient to allow the system to come to equilibrium. Generally, two or three separate tests were performed in a single day. Experiments performed during the long-term phase were similar to those performed

### HIGH AND LOW VOC CONCENTRATIONS



### MEDIUM VOC CONCENTRATION



INTENSIVE-PHASE TEST MATRIX  
FIGURE 7

**TABLE 1**  
**INTENSIVE PHASE OPERATING CONDITIONS**

Operating Parameter	UV/Ozone System		
	Ultrox	WMI	
1. VOC Concentration*:			
a. TCE/CTC	- high	151 µg/L - 250+ µg/L	151 µg/L - 250+ µg/L
	- medium	51 µg/L - 150 µg/L	51 µg/L - 150 µg/L
	- low	MDL - 50 µg/L	MDL - 50 µg/L
b. PCE	- high	16 µg/L - 30 µg/L	16 µg/L - 30 µg/L
	- medium	6 µg/L - 15 µg/L	6 µg/L - 15 µg/L
	- low	MDL - 5 µg/L	MDL - 5 µg/L
2. Ozone Dose:			
	- high	28 mg/L - 50 mg/L	0.85 mg/L - 1.40 mg/L
	- medium	15 mg/L - 26 mg/L	0.35 mg/L - 0.80 mg/L
	- low	9 mg/L - 14 mg/L	0.25 mg/L - 0.31 mg/L
3. Water Flow Rate:			
	- high	55 gpm - 62 gpm	15.6 gpm - 18.5 gpm
	- medium	35 gpm - 42 gpm	12.5 gpm - 15.5 gpm
	- low	18 gpm - 22 gpm	8.0 gpm - 12.0 gpm
4. UV-dose**		550 W-s/L - 3,700 W-s/L	180 W-s/L - 250 W-s/L

\*VOC spiking solution was a homogenous mixture of TCE:CTC:PCE in ratios of 1.0 : 1.0 : 0.1.

\*\*During the intensive-phase, either 100% or 50% of the bulbs were on. The actual UV dose was a function of the flow rate and the percentage of the bulbs on.



**TABLE 2**  
**SUMMARY OF INTENSIVE-PHASE TESTING**

Proposed Test Number ULTROX/WMI	Test Conditions										Number of Times* Test Performed		
	VOC Concentration			Ozone Dose			Flow Rate			UV Intensity			
	H	M	L	H	M	L	H	M	L	100%	50%	ULTROX	WMI
103/242	X			X				X		X			1
105/240	X			X					X	X		1	4
107/238	X				X		X			X			4
109/236	X				X			X		X			5
111/234	X				X				X	X		1	2
113/232	X					X	X			X			2
121/227		X		X					X	X		2	2
122/222		X			X		X			X			3
123/223		X			X			X		X		2 (2)	1
124/224		X			X				X	X			1
125/219		X				X	X			X		2	1
126/220		X				X		X		X			1
130/215			X	X				X		X		1	
131/216			X	X				X			X	1	
132/213			X	X					X	X		2	
133/214			X	X					X		X	2	
136/209			X		X			X		X		2 (2)	
137/210			X		X			X			X	2 (1)	
140/205			X			X	X			X		3 (1)	
141/206			X			X	X				X	3	
142/203			X			X		X		X		1	
143/204			X			X		X			X	1	(1)

\* The values in parentheses represent tests performed during the long-term testing phase.

Note: The number of intensive phase tests proposed was 45 per manufacturer. The number of tests actually performed was 32 for ULTROX and 28 for WMI.

during the intensive phase, except, during long-term monitoring the equipment was left operating (for a specific set of operating conditions) for a much longer period of time (e.g., days). The number of Phase II tests which were completed, and fit into the Phase I test matrix, have been included in parentheses in Table 2. Although all of the originally proposed tests could not be performed, results indicate that the number and variety of tests performed were sufficient to satisfactorily evaluate the capabilities and limitations of both UV/ozone system.

### **Long-Term Phase Testing**

The purpose of the long-term phase of this pilot study was to obtain O&M information about both UV/ozone systems. During this period, several individual tests were performed under various operating conditions. These operating conditions are summarized in Tables 3a and 3b. Each long-term test lasted for a period ranging from 1 to 10 days--sufficient time to generate O&M data. Original plans were to select the optimal operating conditions and allow the UV/ozone systems to run, under those conditions, for approximately two months. However, because of the delays experienced in starting the intensive-phase and lower than expected contaminant removals, it was decided that the long-term experimental plan could be modified to accomplish the objectives of (1) obtaining reliable O&M data and (2) performing as many of the proposed intensive-phase tests as possible with equipment and process modifications.

Towards the end of Phase II, several "special studies" were performed. These tests are denoted in Tables 3a and 3b. For WMI, preliminary results from Phase I indicated low VOC removal efficiencies. Rather than devoting time to gathering detailed O&M costs for their system, WMI was given the opportunity to modify their equipment in hopes of improving its operation. For ULTROX, most of Phase II was spent generating O&M data, but a portion of the time was spent evaluating (1) VOC removal from water pumped by Well #25 (one of the contaminated wells) and (2) the use of hydrogen peroxide in the Ultrox equipment as described below. The setup for the "special studies" are discussed briefly in the following subsection.

### **SPECIAL STUDIES**

As mentioned, several "special studies" were performed with both the WMI and ULTROX UV/ozone systems. Tests performed with WMI's system were very equipment

**TABLE 3a**  
**SUMMARY OF LONG-TERM TESTING**  
**ULTROX**

Test Number	Test Duration (days)	Test Conditions												Special Test	
		VOC Concentration			Ozone Dose				Flow Rate			UV Intensity			
		H	M	L	H	M	L	VL	H	M	L	100%	50%		<50%
301	9.8			X		X				X			X		N
302-A	6.1			X			X		X			X			N
302-B	0.9			X		X				X		X			N
303	0.8			X		X				X		X			Y
304	0.8		X				X			X		X			Y
305	1.0		X					X		X				X	Y
306	2.9		X			X				X		X			N
307	2.8			X		X				X		X			N
308	5.2		X			X				X		X			N
309	3.1		X			X				X			X		N
310	2.7		X			X				X			X		N
311	1.1	X						X		X				X	Y
312	0.8	X						X		X				X	Y
313	0.2	X						X		X		No UV Applied			Y
314	0.9	X						X		X		No UV Applied			Y
315	0.2	X						X		X				X	Y
316	0.9	X						X		X				X	Y

**TABLE 3b**  
**SUMMARY OF LONG-TERM TESTING**  
**WMI**

Test Number	Test Duration (days)	Test Conditions												Special Test	
		VOC Concentration			Ozone Dose				Flow Rate			UV Intensity			
		H	M	L	H	M	L	VL	H	M	L	100%	50%		<50%
401	9.8			X			X			X			X		N
402	0.2*			X	Not Analyzed**						X		X		Y
403	0.1			X	X						X	X			Y
404	0.7			X	X						X	X			Y
405	1.2			X	X				X			X			Y

\* Estimated duration.

\*\* For this test, gas-phase ozone was not applied to the water. Instead, oxygen was bubbled into the water in attempts to generate ozone, in situ, as the oxygen/water solution passed the UV lamps.

specific and were geared towards improving the performance of their treatment system. They were designed primarily to evaluate equipment modifications which were hoped would increase the feed-gas ozone concentrations and improve the ozone mass transfer efficiency through their system. The special studies performed using ULTROX's equipment were more process specific than they were equipment specific. They were designed to (1) compare treatment performance using actual contaminated well water with treatment performance using water from Windsor Reservoir and (2) evaluate overall process performance using other AOPs. Since performance was not greatly improved, equipment modifications made by WMI will not be discussed further.

### **UV/Ozone Treatment of Water from Pasadena Well #25**

Two UV/ozone treatment tests were performed on water pumped by Pasadena's Well #25. (Windsor Reservoir supplied the water for all other tests.) Their purpose was to determine if differences in general water quality between Windsor Reservoir water and water from Well #25 would alter (improve or worsen) previously measured VOC removal efficiencies. Water quality parameters of particular concern were alkalinity, pH, and total organic carbon (TOC); previous AOP research indicated that changes in these parameters can change the UV/ozone processes' ability to destroy synthetic organic chemicals (Glaze, et al., 1987).

Two experiments were performed using water from Well #25. For the first test (#303), no VOCs were spiked into the water and the UV/ozone process was used to treat the actual VOC concentrations in the well water. During the second test, a medium level of VOCs concentrations ( $\text{TCE} \approx 100 \mu\text{g/L}$ ;  $\text{CTC} \approx 100 \mu\text{g/L}$ ;  $\text{PCE} \approx 15 \mu\text{g/L}$ ) were spiked into the water.

### **VOC Destruction Using $\text{H}_2\text{O}_2/\text{O}_3$ and $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$**

In addition to testing the UV/ozone advanced oxidation process (AOP), two other AOPs were tested-- $\text{H}_2\text{O}_2/\text{ozone}$  and  $\text{H}_2\text{O}_2/\text{ozone}/\text{UV}$ . The reasons for testing these other two AOPs were twofold: unsatisfactory CTC removals using UV/ozone alone and economics.

First, preliminary results from Phase I of this study indicated the UV/ozone process was not effective in reducing CTC concentrations to the desired level ( $\leq 2 \mu\text{g/L}$ ). It was thought that another of the AOPs might be able to effectively destroy CTC. In other pilot

investigations (Aieta, et al., 1987),  $H_2O_2$ /ozone was shown to effectively remove both TCE and PCE; however, it is not known to have been tested for CTC removal. The  $H_2O_2$ /ozone/UV AOP process is not known to have been tested prior to this study.

Second, results from a recent  $H_2O_2$ /Ozone pilot work showed the  $H_2O_2$ /ozone process could provide high percent removals of TCE and PCE from a groundwater using relatively low dosages of peroxide and ozone, and a very short contact time (Aieta, et al., 1987). From an economics standpoint, the lower chemical usage and shorter contact time associated with  $H_2O_2$ /ozone treatment could mean substantial savings for the City of Pasadena, in both capital and O&M expenses, for a potentially equal (or perhaps greater) percentage removal of PCE and TCE obtained with UV/ozone treatment. The effectiveness of  $H_2O_2$ /ozone oxidation in removing CTC was not known.

The operating conditions used for both  $H_2O_2/O_3$  and  $H_2O_2/O_3$ /UV tests (#311-316) were:

- o Ozone dose = 4 ppm
- o Peroxide dose = 2 ppm
- o Contact time = 2.2 minutes

For the  $H_2O_2/O_3$ /UV tests, UV doses varying between 0 and 315 watt-sec/L were used.

The approximate VOC spiking concentrations used were 200-, 200-, and 1.5- $\mu$ g/L for TCE, CTC, and PCE, respectively. The hydrogen peroxide dosing solution was fed into the system at a point immediately after the influent sample collection point. To achieve an ozone dose of 4 ppm, the flow rate through the ozone generator had to be greatly reduced, and the flow of ozone routed to the second stage only. The water flow rate was set at approximately 45 gpm, giving an ozone contact time of 2.2 minutes in the second stage only.

In the  $H_2O_2/O_3$ /UV tests, the applied UV dose was controlled by limiting the number of lamps turned on. Initially, the test was carried out with a total of 12 lamps energized in the second chamber. The procedure was then repeated with 6 lamps energized, and again with all the lamps off to give results for the case of  $H_2O_2$ /Ozone oxidation. The series of

three tests just described, were then repeated under the same conditions.

## **SAMPLE COLLECTION**

### **Collection Points**

For all tests done with the ULTROX equipment, the influent and effluent liquid sample collection points were S1 and S2, as shown in Figure 3, respectively. In the WMI UV/ozone studies, the influent and effluent sampling points were S1 and S2, respectively, for both the initial site layout (Figure 4a) and the modified site layout (Figure 4b).

### **Sample Preservation**

Upon collection, liquid samples taken for VOC analyses and oxidation by-products analyses were preserved through the addition of sodium thiosulfate. Samples for TOC analyses were preserved with sulfuric acid. No sample preservation was needed for alkalinity analysis. Ozone, hydrogen peroxide and pH were determined in the field.

## **ANALYTICAL METHODS**

VOCs, TOC, pH, and alkalinity analyses were done on both the influent and effluent samples. Effluent samples were also analysed for residual  $\text{H}_2\text{O}_2$  and residual ozone. A few selected effluent samples were analyzed for oxidation by-products. Both feed gas and off gas were monitored for ozone concentrations.

Standard Methods (16th edition) were used for the determination of pH, alkalinity, and TOC. The EPA gas chromatography/mass spectrometry (GC/MS) method 524.2 for Volatile Organics Analysis was used to determine the VOCs and the oxidation by-products. Due to their unstable nature,  $\text{H}_2\text{O}_2$  and ozone were analyzed immediately at the field site after collection.  $\text{H}_2\text{O}_2$  was determined by a fluorometric technique in which a fluorescent compound was formed between  $\text{H}_2\text{O}_2$ , horseradish peroxidase and p-hydroxyphenylacetic acid (Lazrus et al., 1985). The indigo method was used for the analysis of ozone (Bader and Hoigne, 1982).

## SECTION 4



## SECTION 4

### EXPERIMENTAL RESULTS

In order to understand the results presented in this section, a brief explanation is provided to describe the chemistry driving the advanced oxidation processes.

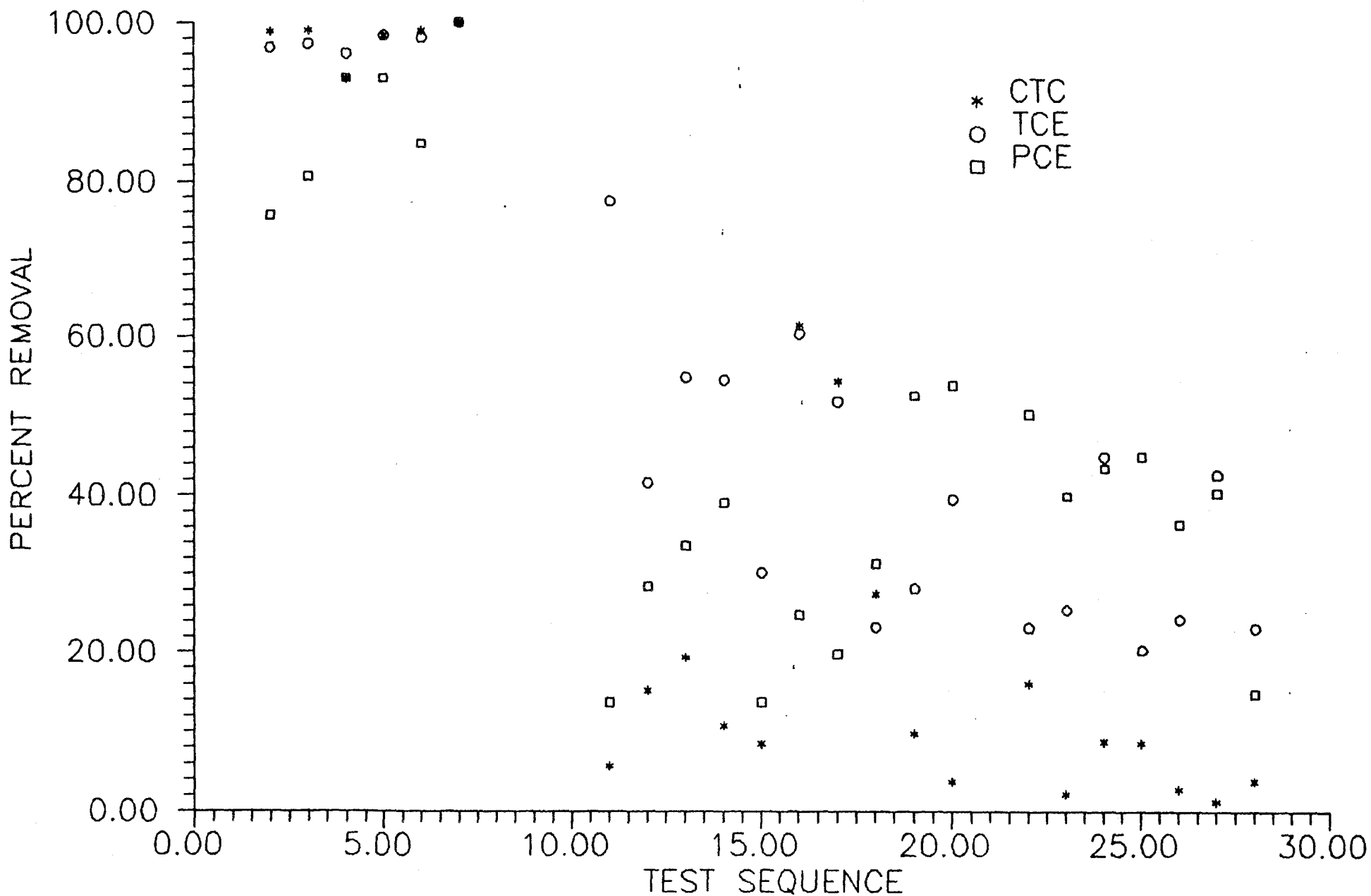
The oxidation of organics in the presence of ozone occurs via two pathways--one involving molecular ozone and the other involving the hydroxyl radical which is formed during the decomposition of ozone. Oxidation via molecular ozone is a highly selective, relatively slow, reaction. Oxidation via the hydroxyl radical, however, is a very rapid and less selective process (Hoigne and Bader, 1983a and 1983b). The advanced oxidation processes promote the formation of hydroxyl radicals. The processes generally considered AOPs include: ozone in a high pH solution,  $H_2O_2$ /ozone, UV/ozone, and  $H_2O_2$ /UV.

Results of the UV/ozone pilot-scale evaluations, along with results of the few  $H_2O_2$ /ozone and  $H_2O_2$ /ozone/UV tests, are discussed in this section.

#### WMI AND ULTROX UV/OZONE OXIDATION SYSTEMS

##### VOC Removal Efficiencies Obtained Using WMI's UV/Ozone System

Results from the first series of tests performed on WMI's system indicated excellent VOC removals (80% - 100% for TCE, PCE, and CTC). However, after completion of these first tests, VOC removal efficiencies dropped off significantly and the high removals could not be reproduced over the duration of the intensive monitoring phase. This trend is depicted in Figure 8 which is a plot of VOC percent removals versus the order in which the tests were performed, or test sequence. Since the high VOC removals seen during the first part of the study could not be repeated during later testing, even under essentially identical operating conditions, these data points were considered erroneous and eliminated from further analysis. Although it is possible that these exceptionally high removals are valid results (because no reasonable explanation for the sudden change in treatment efficiencies can be offered and because the results could not be repeated) it was decided



WATER MANAGEMENT INC.  
PERCENT REMOVAL VS. TEST SEQUENCE  
FIGURE 8

that conclusions about the overall performance of WMI's system should not be based on these numbers alone.

The percentage VOC removals as a function of ozone dose are shown in Figure 9. Although the data are scattered, a general trend of increasing TCE and PCE removal is seen with an increasing ozone dose. The CTC removals remained low for the entire testing period and did not seem to increase with an increasing ozone dose, over the range of ozone doses tested. WMI's treatment system does not include an external ozone supply. Instead, ozone is generated in situ (in the gas phase) in an oxygen stream passes through the UV reactors, prior to being diffused into the water stream. The range of ozone doses tested was the range generated by the WMI system.

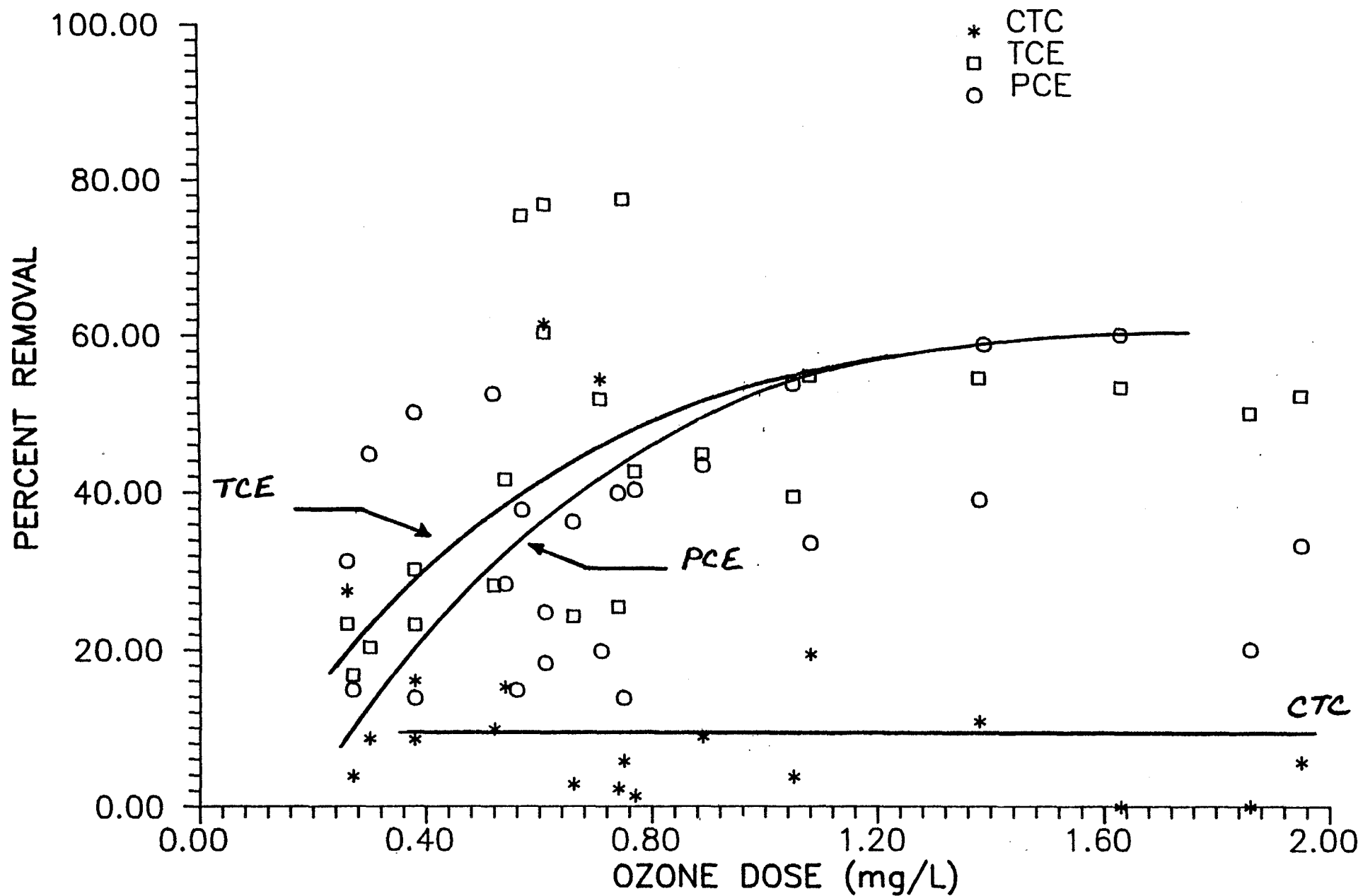
Overall, the WMI UV/ozone system exhibited the ability to provide VOC removal efficiencies on the order of:

<u>Demonstrated Removals</u>	<u>Treatment Goals</u>
TCE = 50% removal	99% removal
PCE = 50% removal	90% removal
CTC = 15% removal	99% removal

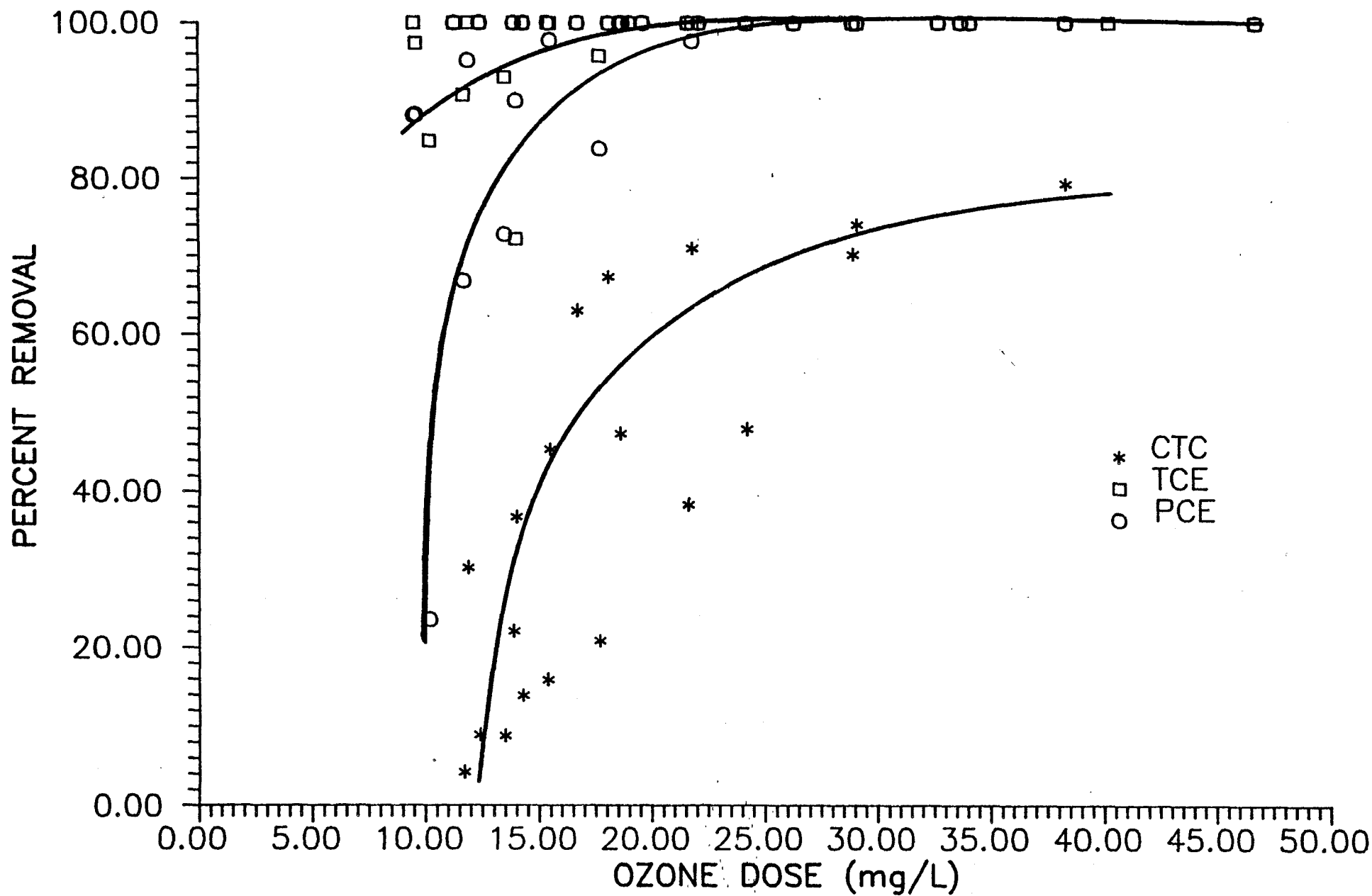
These removals would not provide satisfactory treatment of Pasadena's water at the current VOC concentrations ( $[TCE] \approx 18 \mu\text{g/L}$ ;  $[CTC] \approx 21 \mu\text{g/L}$ ;  $[PCE] \approx 4 \mu\text{g/L}$ ), which are much less than the projected future concentrations. Therefore, from this point on, the WMI UV/ozone system will be dropped from further evaluation and discussion. Revised cost estimates for UV/ozone treatment, presented in a later section of this report, were prepared for the ULTROX system only; the cost of WMI's system was not reevaluated.

#### **VOC Removal Efficiencies Obtained Using ULTROX's UV/Ozone System**

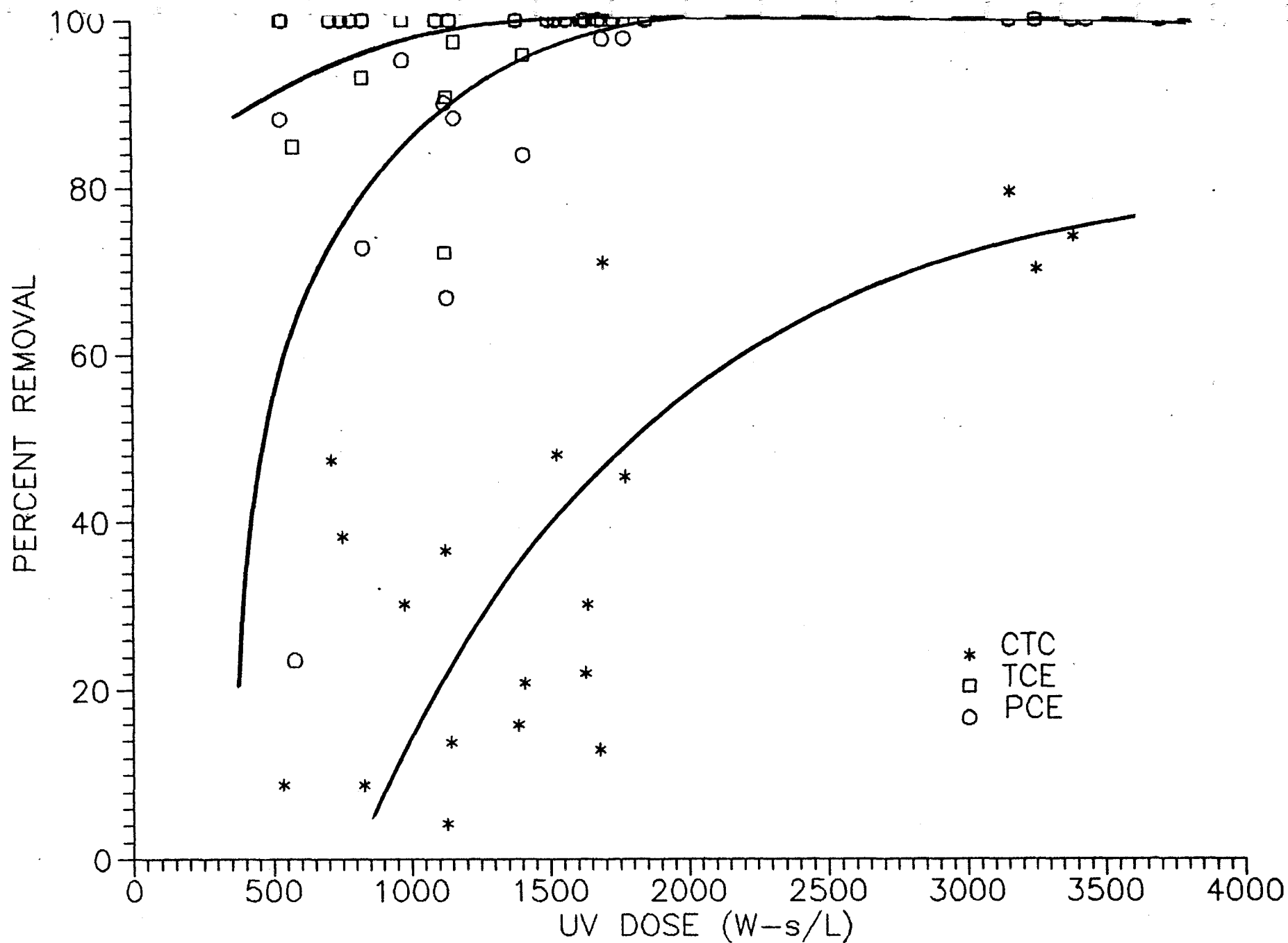
The effectiveness of the UV/ozone oxidation process is a function of UV dose, ozone dose, and contact time. VOC percent removals obtained with ULTROX's UV/ozone system were plotted as a function of applied ozone dose (Figure 10), applied UV dose (Figure 11), and contact time (Figure 12). As shown in Figures 10 through 12, the percentage VOC removal increases as the UV dose, ozone dose, and contact time increase.



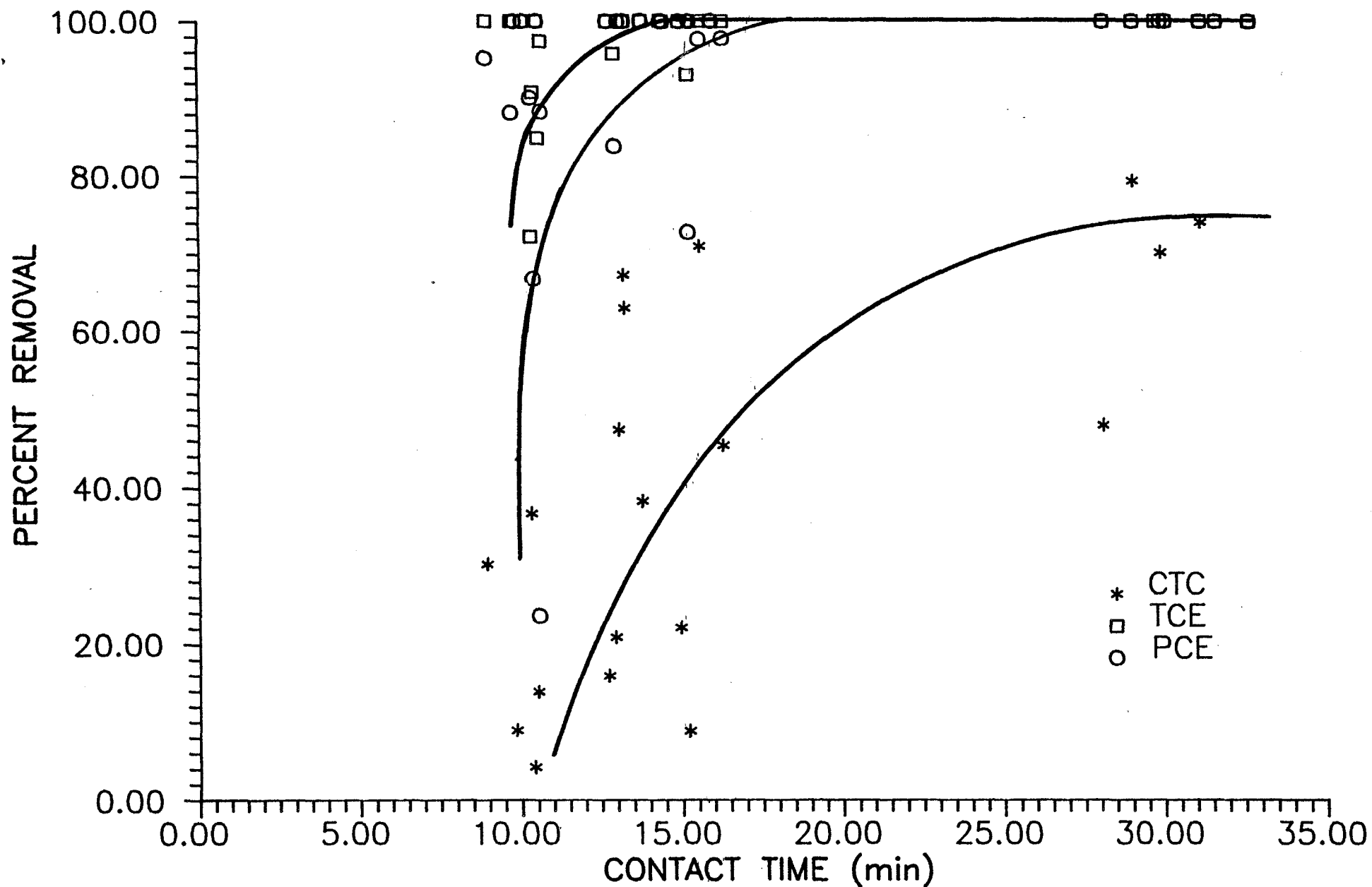
WATER MANAGEMENT INC. PERCENT REMOVAL VS. OZONE DOSE  
FIGURE 9



ULTROX INTERNATIONAL PERCENT REMOVAL VS. OZONE DOSE  
FIGURE 10



ULTROX INTERNATIONAL PERCENT REMOVAL VS. UV DOSE  
FIGURE 11



ULTROX INTERNATIONAL PERCENT REMOVAL VS. CONTACT TIME  
FIGURE 12

The ULTROX UV/ozone system demonstrated excellent TCE and PCE removals. CTC, however, is a much more difficult compound to oxidize and substantially lower percentage removals were attained. Overall, results from the pilot tests indicate that, over the range of VOC concentrations and operating conditions tested, the ULTROX UV/ozone treatment system is capable of providing VOC removals up to:

<u>Demonstrated Removals</u>	<u>Treatment Goals</u>
TCE = 99% removal	99% removal
PCE = 99% removal	90% removal
CTC = 80% removal	99% removal

As indicated by these plots, the optimal operating conditions for attaining 95% - 99% removal of TCE and PCE are:

- o Applied ozone dose  $\approx$  15 mg/L
- o Applied UV dose  $\approx$  1500 watt-sec/L
- o Contact Time  $\approx$  15 minutes

Under these conditions, though, only 50% - 60% CTC removal is attained. Revised cost estimates for a full-scale UV/ozone (ULTROX) treatment facility were prepared using these optimal operating conditions. These costs are presented in a later section.

### **Comparison of the Two UV/Ozone Systems Tested**

Results of the intensive monitoring phase indicate that much higher TCE, PCE, and CTC removals can be achieved with ULTROX's system than with WMI's. Even under the current levels of contamination, WMI's system will not provide adequate treatment for TCE, PCE, or CTC and ULTROX's system will not provide adequate treatment for CTC. (The treatment goal is 2  $\mu$ g/L for each VOC.) The treatment levels attainable for the current VOC concentrations at Well #25 are summarized in Table 4.

In summary, WMI's UV/ozone system has been dropped from the list of viable treatment alternatives because it has not demonstrated sufficient removal of VOCs. Ultrox's system has demonstrated excellent treatment for TCE and PCE, but was not effective for CTC.



TABLE 4

## ATTAINABLE TREATMENT LEVELS FOR CURRENT CONTAMINANT LEVELS

VOC	Current Conc. at Well #25	WMI		ULTROX	
		Attainable Percent Removals	Treated Effluent Concentrations	Attainable Percent Removals	Treated Effluent Concentrations
TCE	18 µg/L	50%	9 µg/L	99%	< 2 µg/L
PCE	4 µg/L	50%	2 µg/L	99%	< 2 µg/L
CTC	21 µg/L	15%	18 µg/L	80%	4 µg/L

## **ALTERNATE ADVANCED OXIDATION PROCESSES (AOP)**

Recent JMM pilot work demonstrated excellent TCE and PCE removals using  $\text{H}_2\text{O}_2$ /ozone oxidation. These tests also showed that the required ozone dose was much less than for UV/ozone oxidation. When the revised cost estimates for full-scale UV/ozone treatment indicated how expensive it actually would be, several  $\text{H}_2\text{O}_2$ /ozone tests were performed to see if an equivalent, or better, degree of treatment could be attained with a potentially less expensive AOP. All of these "special studies" were performed using ULTROX's equipment. Results from these tests are presented in the following paragraphs.

### **VOC Removal Efficiencies Obtained Using $\text{H}_2\text{O}_2/\text{O}_3$ Oxidation**

The VOC removal efficiencies obtained using  $\text{H}_2\text{O}_2$ /ozone oxidation are compared with those obtained using UV/ozone oxidation in Table 5. The  $\text{H}_2\text{O}_2$ /ozone test results included in this table are from the only two tests performed. The UV/ozone results included were selected because their influent VOC concentrations were in the same range as were used for the  $\text{H}_2\text{O}_2$ /ozone tests.

As indicated by these data,  $\text{H}_2\text{O}_2$ /ozone requires substantially less ozone and a much shorter contact time than UV/ozone, and provides essentially the same degree of treatment for TCE and CTC (>99% and 60%, respectively). However, under these operating conditions, UV/ozone seemed to provide more effective treatment of PCE than did  $\text{H}_2\text{O}_2$ /ozone (>99% versus 75%). Researchers studying the UV/ozone oxidation of PCE (Peyton, et al., 1982 and Glaze, et al., 1987) found that PCE absorbs (weakly) ultraviolet radiation at 254 nm, which weakens the bonds holding the PCE molecule together and accelerates its decay. The limited data from this study concur with these findings since best PCE removals were attained in the presence of ultraviolet light.

### **VOC Removal Efficiencies Obtained Using $\text{H}_2\text{O}_2/\text{O}_3$ /UV Oxidation**

A limited number of tests were performed using constant peroxide and ozone dosages in conjunction with varying UV dosages. The purpose was to determine whether or not ultraviolet light would increase the generation of hydroxyl radicals, thereby increasing the overall effectiveness of the oxidation process. The peroxide and ozone doses were maintained constant at 2 mg/L and 4 mg/L, respectively. UV doses were varied from

TABLE 3  
COMPARISON OF H<sub>2</sub>O<sub>2</sub>/OZONE AND UV/OZONE  
VOC REMOVAL EFFICIENCIES

Item	Treatment Processes				
	UV/Ozone <sup>a</sup>			H <sub>2</sub> O <sub>2</sub> /Ozone <sup>b</sup>	
	Trial 1	Trial 2	Optimum	Trial 1	Trial 2
Influent VOC Concentrations:					
TCE	170 µg/L	159 µg/L	NA	110 µg/L	220 µg/L
PCE	16.8 µg/L	15.8 µg/L	NA	1.2 µg/L	1.4 µg/L
CTC	225 µg/L	211 µg/L	NA	160 µg/L	220 µg/L
Ozone Dose	28.9 mg/L	24.2 mg/L	15 mg/L	3.9 mg/L	4.3 mg/L
Contact Time	30 min.	28 min.	15 min.	2.2 min.	2.4 min.
Percent Removals:					
TCE	>99%	>99%	>99%	>99%	>99%
PCE	>99%	>99%	95%	75%	79%
CTC	72%	48%	50%	51%	67%

<sup>a</sup> Trial 1 represents test #128 which was performed on 7/2/87. Trial 2 represents test #129 which was also performed on 7/2/87. These tests were selected for comparison because their influent VOC concentrations were similar to those used for the H<sub>2</sub>O<sub>2</sub>/Ozone tests.

<sup>b</sup> Trial 1 represents test #313, performed on 11/11/87. Trial 2 represents test #314, performed on 11/12/87.

NA = Not applicable. Optimum operating conditions were determined from Figures 10-12, which are independent of VOC concentration.

zero to 300 watt-sec/L. Results of these tests are summarized in Table 6 and illustrated in Figure 13.

It is difficult to draw conclusions from so few data points. However, the data do indicate that UV light does not improve the oxidizing capabilities of the  $\text{H}_2\text{O}_2$ /ozone process; if anything, UV irradiation hinders VOC removal. For example, the removal efficiencies of TCE trend to decrease with increasing UV dose. For PCE and CTC, though, this relationship is not readily apparent.

Although these data do not show a conclusive relationship between UV dose and percent VOC removal, the existence of such a relationship could easily be rationalized. Researchers (Stachelin and Hoigne, 1982; Forni, et al., 1982) have shown that peroxide can act both as a source and sink for the hydroxyl radicals. The series of chain reactions describing ozone decomposition in the presence of peroxide indicate that an optimum stoichiometric ratio (ratio of the number of moles of reactants and products in the chemical equation) of peroxide:ozone exists which maximizes hydroxyl radical formation. At the same time, the photolysis of ozone in water results in the formation of peroxide. Thus, when UV light, ozone, and peroxide are used in combination, the photolysis of ozone generates peroxide which changes the ratio of peroxide:ozone. This excess peroxide (the amount in excess of the optimum ratio) acts as hydroxyl radical scavengers, thereby reducing the number of radicals available to destroy VOCs.

In addition, UV light can cause breakdown (auto-catalytic decay) of ozone in the gas-phase before the ozone dissolves into the liquid-phase (water). As an alternative explanation, the results in Table 6 could indicate that the UV light is decomposing the ozone in the gas-phase, thereby decreasing the effective ozone available for TCE, PCE, and CTC oxidation in the liquid-phase. Whatever the reason, UV irradiation does not improve the oxidizing capabilities of the  $\text{H}_2\text{O}_2/\text{O}_3$  process, under the conditions tested.

## **OXIDATION BY-PRODUCTS**

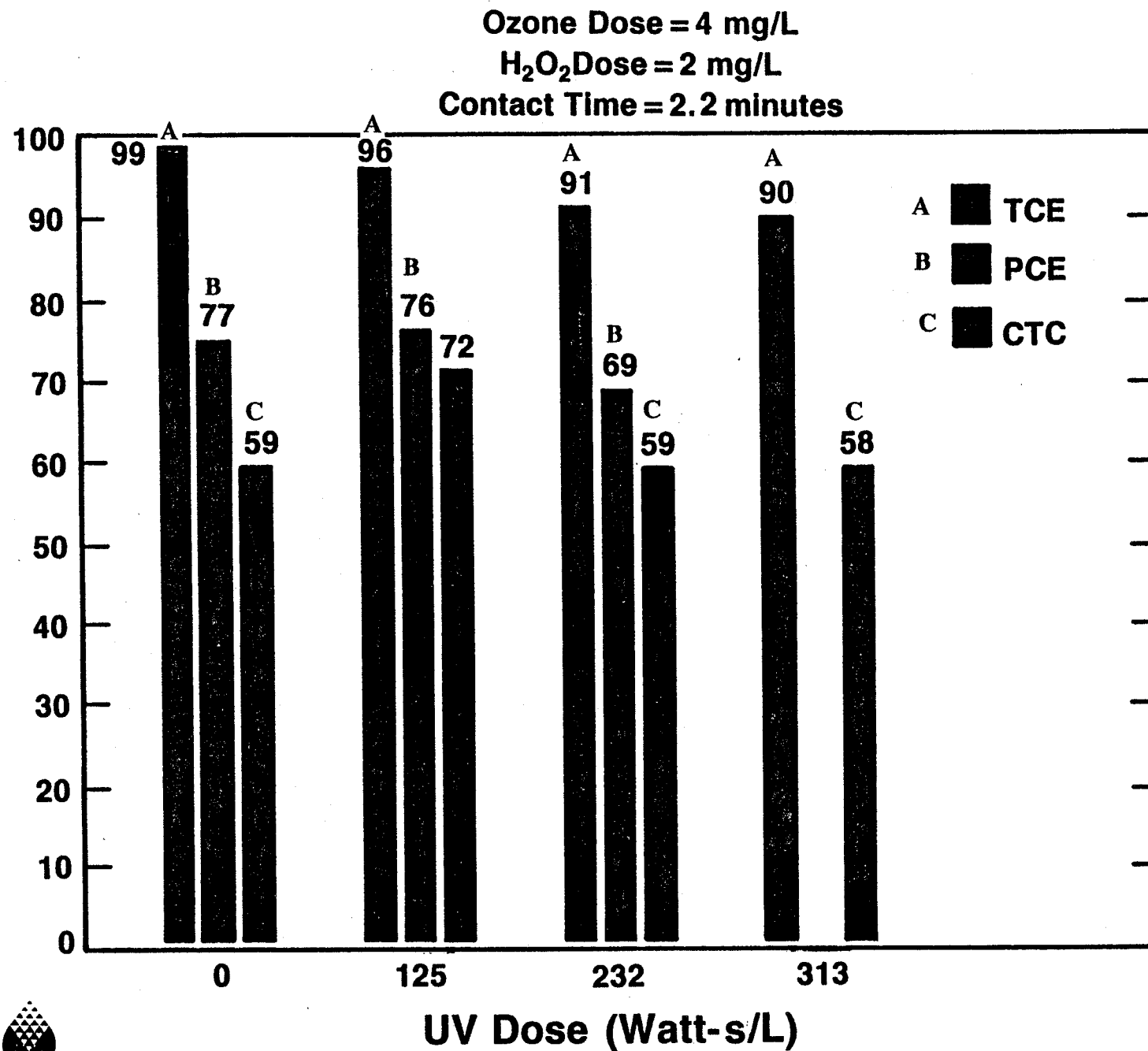
The principal end-products of VOC oxidation, when complete oxidation is attained, theoretically should be carbon dioxide, water, and chloride. Incomplete oxidation,

TABLE 6

VOC REMOVALS ATTAINED USING  $H_2O_2$ /OZONE OXIDATION  
IN CONJUNCTION WITH VARYING UV DOSAGES

UV Dose	----- VOC Removals -----		
	TCE	PCE	CTC
0 watt-sec/L	>99%	77%	59%
125 watt-sec/L	96%	76%	72%
232 watt-sec/L	91%	69%	59%
313 watt-sec/L	90%	---*	58%

\* No data for this test.



VOC REMOVALS WITH H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV  
FIGURE 13

however, may result in the formation of other organic by-products. Therefore, several effluent water and off-gas (WMI only) samples were analyzed for "other" organic by-products which possibly could have been formed as a result of incomplete oxidation of the VOCs. Most of the potential by-products are volatile organics. Thus, the standard analytical methodologies for measuring VOCs were employed for by-product analysis. The list of potential by-products which are amenable to the VOC analytical methodologies include: tetrachloroethene epoxide; mono-, di-, and tri-chloroacetal isomers; and phosgene. The potential by-products not amenable to this type of analysis include: mono-, di-, and tri-chloroacetic acid isomers; chlorinated ethanediols; and chlorohydroxyacetal isomers.

No oxidation by-products were detected in any of the samples analyzed. The detection limit for most of these compounds is expected to be between 1  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$ .

## **LONG-TERM PHASE TESTING RESULTS**

As discussed earlier, the long-term phase testing was modified to include several studies lasting between 1-10 days which accomplished the objectives of (1) obtaining reliable O&M data, and (2) performing as many of the proposed intensive-phase tests as possible. The following O&M issues were experienced during the pilot studies which could reflect potential problems that might arise in the full scale treatment facility.

For the Ultrox system, the majority of the problems were associated with ozone generation. The most frequent failure was associated with the air drying unit which, because of the moist air, resulted in a lower production of ozone. One ozone generator cell had to be replaced and another repaired. Nearing the end of the project, several bulbs had severely deteriorated, and had a dull purple color as opposed to the brightness of a new bulb. Instability of the ozone gas flow meters was another difficulty experienced.

In the WMI system, there were several breakages of the quartz sheath around the UV lamp but the cause remained unknown. Early problems with overheating of the oxygen compressor required its replacement with bottled pure oxygen.

## **SUMMARY OF VOC REMOVAL EFFICIENCIES**

To summarize the results of this study, the following can be said:

- o The performance of the ULTROX UV/ozone system in degrading TCE, PCE, and CTC was superior to that of the WMI UV/ozone system.
- o The  $H_2O_2$ /ozone AOP demonstrated essentially identical TCE and CTC removals, and only marginally lower PCE removal, as did the UV/ozone AOP, but used a substantially lower ozone dose and shorter contact time.
- o The combined usage of UV light, ozone, and peroxide, did not improve VOC removal efficiencies.
- o Similar VOC removal efficiencies were obtained when treating contaminated well water, as when treating water from Windsor Reservoir that had been spiked with VOCs.



**SECTION 5**

## SECTION 5

### REVISED COST ESTIMATES FOR FULL-SCALE, LIQUID-PHASE, AOP TREATMENT

Cost estimates for the design, construction, and operation of a full-scale (1) UV/ozone and (2)  $\text{H}_2\text{O}_2$ /ozone treatment facility were prepared using information learned from the pilot study and are presented in the following paragraphs. Preliminary cost estimates for UV/ozone treatment were included in the Treatability/Feasibility Report, using design and operation information supplied by the manufacturer prior to pilot testing. Estimates in that report were for both the ULTROX and WMI treatment systems. The revised UV/ozone cost estimates presented in this report are representative of ULTROX's system only; results from the pilot study indicated WMI's system could not, reliably, provide satisfactory VOC removal--even for TCE and PCE which are relatively easily oxidized. Cost estimates for  $\text{H}_2\text{O}_2$ /ozone treatment were not included in the Treatability/Feasibility Report because it is a new process and, at the time, was not known to have been tested at the pilot level for VOC removal, much less in a full-scale treatment application. Thus, the figures for  $\text{H}_2\text{O}_2$ /ozone treatment are "first time" estimates rather than revised estimates.

General assumptions and design criteria used in determining the cost of UV/ozone (ULTROX) and  $\text{H}_2\text{O}_2$ /ozone treatment are listed in Table 7. These are design criteria and operating requirements based on results of the pilot study. From the modified long-term phase testing, the average power consumption for ozone generation, destruction, and gas recycle were determined to be 18.8 KWH/lb  $\text{O}_3$  (Table 7). This power requirement was incorporated in the total annual O&M cost estimate given in Table 8. The revised estimates for the ULTROX UV/ozone system are feasibility level estimates, meaning that the accuracy is plus 50% or minus 30% of the actual costs. However, the estimates for  $\text{H}_2\text{O}_2$ /Ozone treatment should be assumed less accurate since the process has not yet been optimized for Pasadena's water and a full-scale facility has never been built.

#### UV/OZONE

The design criteria used for estimating the cost of UV/ozone (ULTROX) treatment are

TABLE 7

## ASSUMPTIONS AND DESIGN CRITERIA USED FOR COST ESTIMATIONS

## General

---

Flow Rate	=	4155 GPM
Pump Usage	=	67% (20 days/mo)
Amortization Period	=	20 years
Interest Rate*	=	8%
Power Cost*	=	\$ 0.074/KWH
Labor Rate (including overhead)*	=	\$ 26.25/hr

ULTROX-UV/O<sub>3</sub> (initial costs)

Ozone Dose	=	21 mg/L
UV Dose	=	2040 watt-sec/L
Contact Time	=	5 minutes
Power Consumption for Ozone Generation (according to manufacturer)	=	8.5 KWH/lb O <sub>3</sub> (or \$0.11/thous gal.)

ULTROX-UV/O<sub>3</sub> (revised costs)

Ozone Dose	=	15 mg/L
UV Dose (power supplied to bulb)	=	1500 watt-sec/L
Contact Time	=	15 min
Power Consumption for O <sub>3</sub> Generation** (based on industrial average)	=	18.8 KWH/lb O <sub>3</sub> (10 KWH/lb O <sub>3</sub> )

H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>

Ozone Dose	=	4 mg/L
Hydrogen Peroxide Dose	=	2 mg/L
Contact Time	=	3 min
Power Consumption for O <sub>3</sub> Generation (based on industrial average)	=	10 KWH/lb O <sub>3</sub>

---

\* Information supplied by the City of Pasadena.

\*\* The power consumption of 18.8 KWH/lb O<sub>3</sub> was based on the pilot study results. Since the pilot scale ozone generators possibly consume more power than ozone generators in a full-scale application, cost estimates were also made using the industrial average power consumption of 10 KWH/lb O<sub>3</sub> shown in parenthesis.

TABLE 8

**COST ESTIMATE FOR FULL-SCALE UV/OZONE TREATMENT  
USING THE ULTROX TREATMENT SYSTEM**

ITEM	COST
<b>Capital Costs:</b>	
UV/Ozone Treatment Units (customized facility <sup>a</sup> )	\$ 2,100,000
Building	492,000
Concrete Pad	149,000
Electric Hookup	40,000
Yard Piping	93,500
Operator Training	1,500
Pump Station	64,000
Construction <sup>b</sup>	882,000
<b>Total Capital</b>	<b>\$ 3,822,000</b>

**Operation & Maintenance Costs:**

Ozone Generation	\$ 255,000 (136,000)
UV Generation	255,000
Maintenance Materials & Labor	12,000
Lamp Replacement	59,000
<b>Total Annual O&amp;M</b>	<b>\$ 581,000 (462,000)</b>

**Summary of Annual Costs<sup>c</sup>:**

Amortized Capital (A/P, 8%, 20)	\$ 389,000
Annual O&M	581,000 (462,000)
Total Annual	970,000 (851,000)
Unit Cost - \$/10 <sup>3</sup> Gal.	0.66 (0.58)
Unit Cost - \$/AF	216 (190)

<sup>a</sup> Cost obtained through telephone quote from Ultrox representative.

<sup>b</sup> Construction cost includes: contingency (10%), contractors overhead and profit (15%), and interest during construction (5%).

<sup>c</sup> The numbers in parentheses were based on ozone power consumption of 10 KWH/lb O<sub>3</sub>, which is the industrial average. The other numbers were based on pilot study resultant power consumption of 18.8 KWH/lb O<sub>3</sub>.

listed in Table 7. The required UV dose, ozone dose, and contact time were determined from the pilot data, as presented in Figures 10, 11, and 12, and are sufficient to provide 99% and 95% removals of TCE and PCE, respectively. At these operating conditions, CTC removal is between 25% and 55%. Results from the pilot work indicate that up to 80% CTC removal can be attained, but the required UV/ozone doses and contact time would be greater than what is listed in Table 7. Thus, for cost estimation purposes, the contact time and dosages which provide almost complete removal of TCE and PCE were selected, even though CTC oxidation is incomplete. Additionally, these design parameters were assumed independent of initial VOC concentration.

The revised costs for UV/ozone (ULTROX) treatment are presented in Table 8. A comparison with the initial costs presented in the Treatability/Feasibility Report is as follows:

<u>Item</u>	<u>Original Estimate</u>	<u>Revised Estimate*</u>
Capital	\$ 2,900,000	\$ 3,822,000
Annual O&M	\$ 270,000/yr	\$ 580,000/yr (\$462,000/yr)
Unit Cost	\$ 126/AF	\$ 216/AF (\$190/AF)

\* Costs in parentheses were determined using power consumption for ozone generation based on an industrial average of (10 KWH/lb O<sub>3</sub>). Numbers outside of parentheses were based on ozone generation power consumption determined from pilot study (18.8 KWH/lb O<sub>3</sub>).

There are substantial differences in both capital and annual O&M costs between the initial and revised estimates. Changes in design criteria between these two ULTROX cost estimates are summarized in Table 7. Results from the pilot study indicated that a retention time of at least 15 minutes would be required. This is three times longer than what was originally estimated. Consequently, more UV/ozone treatment units or several large customized facilities will be required. This explains the increase in capital cost in the revised estimate. The higher revised O&M cost estimate is mainly due to the higher power consumption for ozone generation. From the pilot study, a power consumption for ozone generation of 18.8 KWH/lb O<sub>3</sub> is found, and this is significantly higher than the 8.5 KWH/lb O<sub>3</sub> used in the original estimate. However, the manufacturer felt that the power consumption for ozone generation, could be lowered from 18.8 KWH/lb O<sub>3</sub> to 10 KWH/lb O<sub>3</sub> in a totally optimized, full-scale treatment system.

## **H<sub>2</sub>O<sub>2</sub>/OZONE**

The cost of a full-scale H<sub>2</sub>O<sub>2</sub>/ozone treatment facility was estimated, for comparison with the cost of UV/ozone treatment. These costs are summarized in Table 9. In comparison with UV/ozone treatment:

<u>Item</u>	<u>H<sub>2</sub>O<sub>2</sub>/Ozone Treatment</u>	<u>UV/Ozone Treatment</u>
Capital	\$ 390,000	\$ 3,822,000
Annual O&M	\$ 81,000/yr	\$ 580,000/yr
Unit Cost	\$ 27/AF	\$ 216/AF

Although only limited testing was done with H<sub>2</sub>O<sub>2</sub>/ozone treatment, preliminary results indicate this process is equally as effective for TCE and PCE removal as UV/ozone, and substantially less expensive. A summary of the pros and cons associated with these two AOP treatment methods is found in Table 10.

## **COMPARISON OF ESTIMATED TREATMENT COSTS**

The revised cost estimate for UV/ozone (ULTROX) treatment and the estimate for H<sub>2</sub>O<sub>2</sub>/ozone treatment are compared with the estimated treatment costs presented in the Treatability/Feasibility Report, in Table 11. This comparison indicates that H<sub>2</sub>O<sub>2</sub>/ozone is an inexpensive treatment process; its unit cost is approximately the same as the unit cost for air stripping alone. The order of the various treatment processes, from least expensive to most expensive is:

<u>Treatment Process</u>	<u>Unit Cost (\$/AF)</u>
Air Stripping	22
Peroxide/Ozone	27
Air Stripping + GAC-APC	104
GAC	130
UV/Ozone (ULTROX)	216

A summary of the feasibility of the various treatment alternatives is provided in Table 12.

TABLE 9

## COST ESTIMATE FOR FULL-SCALE PEROXIDE/OZONE TREATMENT

ITEM	COST
<b>Capital Costs:</b>	
Contactor	\$ 21,500
Yard Piping	29,200
Chemical Feed Pumps	2,000
H <sub>2</sub> O <sub>2</sub> Storage Tank	3,000
Ozone Generator	176,800
Process Piping	7,000
Electrical	25,000
Control System	17,000
Mechanical Work	10,000
Construction*	95,600
<b>Total Capital</b>	<b>\$ 387,100</b>
<b>Operation &amp; Maintenance Costs:</b>	
Ozone Generation	\$ 36,200
Hydrogen Peroxide	26,400
Maintenance Materials and Labor	16,700
Lab Analyses	2,000
<b>Total Annual O&amp;M</b>	<b>\$ 81,300</b>
<b>Summary of Annual Costs:</b>	
Amortized Capital (A/P, 8%, 20)	\$ 39,400
Annual O&M	81,300
Total Annual	120,700
Unit Cost - \$/10 <sup>3</sup> Gal.	0.08
Unit Cost - \$/AF	27

\* Construction cost includes: contingency (10%), contractors overhead and profit (15%) and interest during construction (5%).

TABLE 10

PROS AND CONS OF THE TWO AOP TREATMENT SYSTEMS  
(UV/OZONE VS. PEROXIDE/OZONE)

ISSUE	UV/OZONE	PEROXIDE/OZONE
Capital Cost	\$ 3,822,000	\$ 390,000
Total Annual Cost	\$ 970,000	\$ 121,000
Versatility - Contaminant Removal		
TCE	99%	99%
PCE	95%	88%
CCl <sub>4</sub>	50%	65%
Space Requirement	12,000 ft <sup>2</sup>	1,000 ft <sup>2</sup>



TABLE 11

COMPARISON OF ESTIMATED TREATMENT COSTS FOR  
SEVERAL ALTERNATIVE TREATMENT PROCESSES

Treatment Alternative	Total Capital Cost (\$)	Annual O&M Cost (\$/Yr)	Total Annual Cost (\$/Yr)	Unit Cost (\$/AF)
Air Stripping	\$ 550,000	\$ 44,000	\$ 100,000	22
H <sub>2</sub> O <sub>2</sub> /Ozone	387,000	81,000	121,000	27
Air Stripping and GAC Air Pollution Control	1,200,000	340,000	460,000	104
Granular Activated Carbon (GAC)	1,950,000	380,000	580,000	130
UV/Ozone (Ultrox, revised)*	3,822,000	581,000 (462,000)	970,000 (851,000)	216 (190)

\* Numbers in parentheses were based on O<sub>3</sub> power consumption of 10 KWH/lb O<sub>3</sub> which is the industrial average.

TABLE 12

## QUALITATIVE SUMMARY OF THE FEASIBILITY OF SEVERAL VOC TREATMENT PROCESSES

Feasibility Category	Air Stripping with GAC-APC	GAC	UV/Ozone Oxidation	Peroxide/Ozone Oxidation
Proven Effectiveness in Full-Scale Treatment Facility	It has been used to effectively remove > 99% of the VOCs (TCE, PCE, and CTC) from water. Although effective, GAC-APC has been used in only a limited number of full-scale contaminated groundwater applications. Not effective for non-volatile compounds.	Proven effective in full-scale application numerous times. Can achieve > 99% VOC (TCE,PCE,CTC) removal. Is effective for the removal of both volatile and non-volatile organics.	Is not known to have been used, on a full-scale, to treat VOC contaminated drinking water. It has been used effectively in industrial applications.	It is not known to have been used in a full-scale treatment application.
Proven Effectiveness in Pilot-Scale Treatment System	Has been proven effective on the pilot-scale. Full-scale systems have been designed and constructed. This is a proven technology.	Has been proven effective on the pilot-scale. A significant amount of research has been done on liquid-phase GAC adsorption. This is a proven technology.	Has been shown to effectively remove up to 99% TCE, 99% PCE, and 80% CTC when VOC concentrations of the contaminated water are < 200 µg/L for TCE and CTC, and < 20 µg/L for PCE. Long retention times are required.	Has been proven effective on the pilot-scale for removing up to 99% TCE, 88% PCE, and 65% CTC when the VOC concentrations of the contaminated water are < 200 µg/L for TCE and CTC, and < 20 µg/L PCE. H <sub>2</sub> O <sub>2</sub> /ozone treatment requires < 1/3 the amount of ozone required for UV/ozone treatment, to provide an approximately equivalent degree of treatment.
Constructability	Easily installed, shop fabricated equipment.	Easily installed, shop fabricated equipment.	Manufacturer claims easy installation. Much of the equipment is shop fabricated.	Never known to have been built on a full-scale. However, the process design is simple so construction should be easy.
Environmental Impacts	Spent carbon is a hazardous material and requires proper disposal.	Spent carbon is a hazardous material and requires proper disposal.	The process does not involve transferring VOCs from one medium to another. No oxidation by-products were detected in pilot investigation. Thus, there should be no environmental impacts.	The process does not involve transferring VOCs from one medium to another. If complete oxidation is achieved, there will be no environmental impacts.

## SECTION 6

## SECTION 6

### ALTERNATIVE TREATMENT SCENARIOS

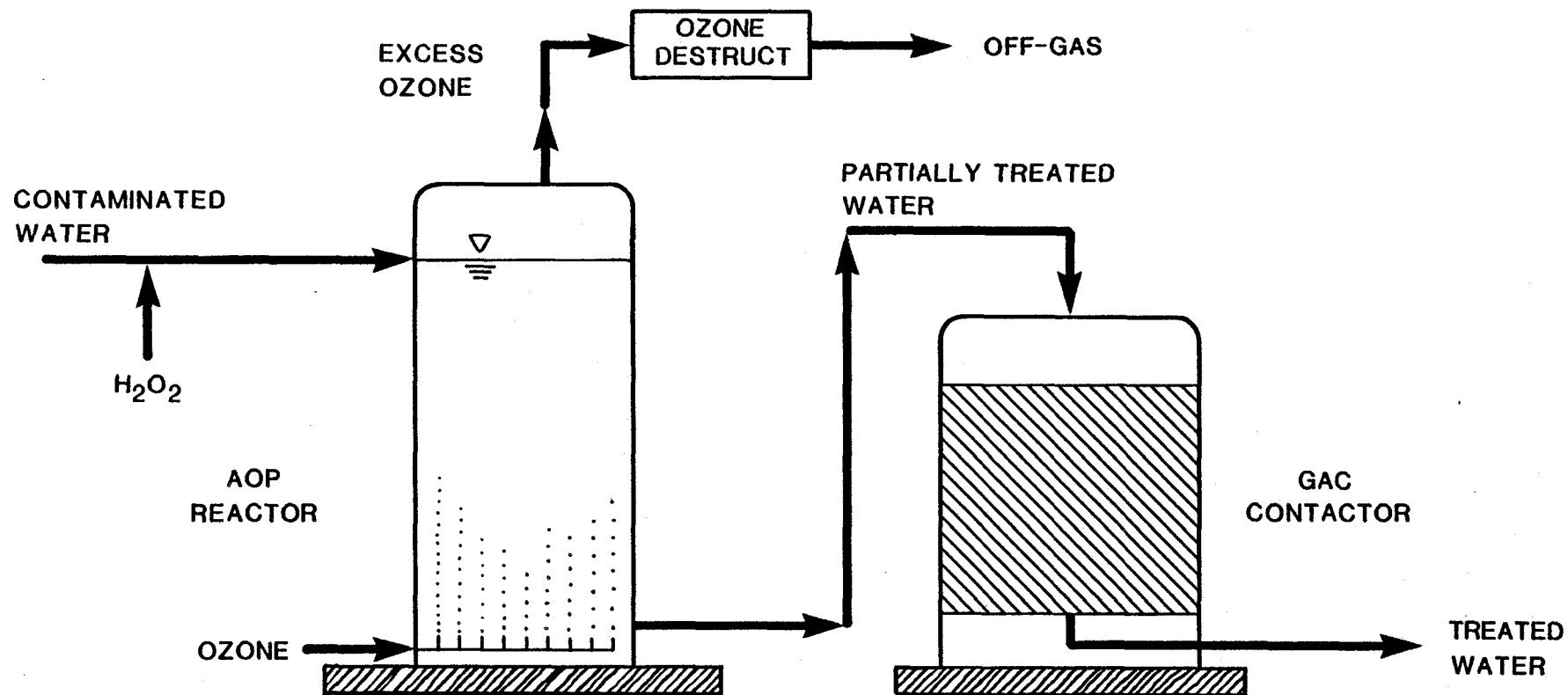
Since the time the Treatability/Feasibility Report was completed, two very new alternative treatment processes have been developed which may meet the City of Pasadena's treatment needs more effectively and less expensively than was demonstrated by liquid-phase UV/ozone oxidation. These two processes--liquid-phase  $H_2O_2$ /ozone and gas-phase AOP--have been tried at either the bench- or pilot-level and appear to be promising technologies. Some of the treatment scenarios that will be discussed are a combination of one of these new AOPs with one or more of the processes identified in the Treatability/Feasibility report. A description of each treatment scenario, along with associated advantages and disadvantages, are presented in the following subsections. Cost estimates have been prepared for the design, construction, and operation of each of these alternative treatment scenarios and are presented in the last subsection. Lastly, these costs are compared with the estimates for (1) air stripping alone, (2) air stripping plus gas-phase carbon adsorption, (3) liquid-phase carbon adsorption, (4) UV/ozone oxidation (revised costs for the ULTROX system), and (5) liquid-phase  $H_2O_2$ /ozone oxidation.

#### LIQUID-PHASE AOP WITH LIQUID-PHASE GAC

A schematic diagram of this treatment scenario is provided in Figure 14. Under this scenario, the  $H_2O_2$ /ozone process is used to first remove 95% or more of the TCE, 50%-70% of the CTC, and 70%-90% of the PCE. This partially treated water then passes through a granular activated carbon (GAC) contactor where the VOCs remaining in the liquid-phase adsorb onto the carbon and are removed from the water. By removing a large percentage of the VOCs prior to carbon adsorption, the adsorption capacity and lifetime of the carbon can be increased substantially.

Excluding economics, which will be discussed later, some of the advantages of this treatment scenario are:

- o Using an AOP to reduce the VOC load passing through the carbon bed may extend the life of the carbon by 50 or 60 percent, as compared with using only liquid-phase carbon adsorption (no AOP pretreatment).



LIQUID-PHASE AOP WITH LIQUID-PHASE GAC

FIGURE 14

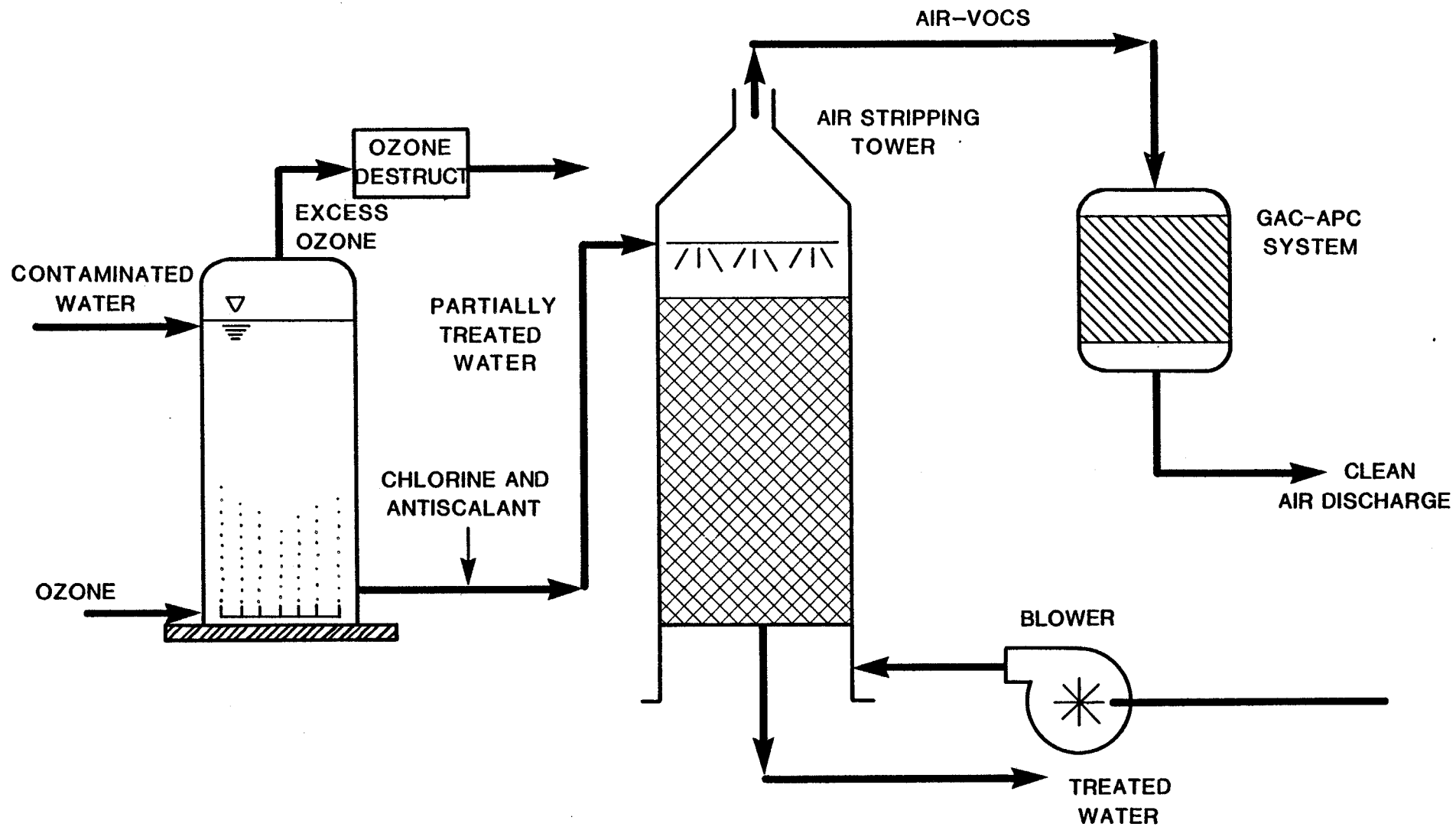
- o There are no associated air pollution problems.
- o It will effectively remove all three VOCs from Pasadena's water.
- o The design for the  $H_2O_2$ /ozone system is reasonably simple. Thus, the maintenance requirements should be very few in comparison with those associated with the UV/ozone system.
- o The equipment used has a fairly low profile (carbon adsorption unit is approximately 20 ft. tall) and is relatively quiet.

The only disadvantage of this scenario is:

- o VOCs not destroyed by the AOP will be transferred to the carbon as the water flows through the carbon contactor. Once breakthrough has been reached, the spent carbon will have to be removed from the site, by a licensed carrier, and hauled away for disposal or regeneration. The spent carbon would be considered hazardous material.

## **LIQUID-PHASE AOP WITH AIR STRIPPING AND GAS-PHASE GAC**

A schematic of this treatment scenario is shown in Figure 15. As shown, the water first goes through  $H_2O_2$ /Ozone oxidation, where a large percentage of the VOC load is destroyed (the same percent reductions described under the preceding treatment scenario). Following AOP oxidation, the water flows through a stripping tower where the VOCs remaining in the liquid-phase are transferred to the gas-phase and exhausted out the top of the tower. The exhaust gas passes through a bed of activated carbon where the VOCs adsorb onto the carbon and are removed from the exhaust gas. This scenario is essentially the same as the Air Stripping/GAC-APC treatment alternative described in the Treatability/Feasibility Report, except that  $H_2O_2$ /Ozone is used to remove most of the TCE and about half of the CTC before air stripping in order to extend the life of the carbon in the air pollution control (APC) system.



LIQUID-PHASE AOP WITH AIR STRIPPING PLUS GAC AIR POLLUTION CONTROL  
FIGURE 15

The advantages of this process are:

- o It increases the life of the carbon bed in the APC system, thereby reducing the annual operation and maintenance costs.
- o There are no associated air pollution problems.
- o It will effectively remove all three VOCs of concern.
- o Much less carbon is required when it is used on the gas-phase as opposed to the liquid-phase.

The disadvantages are:

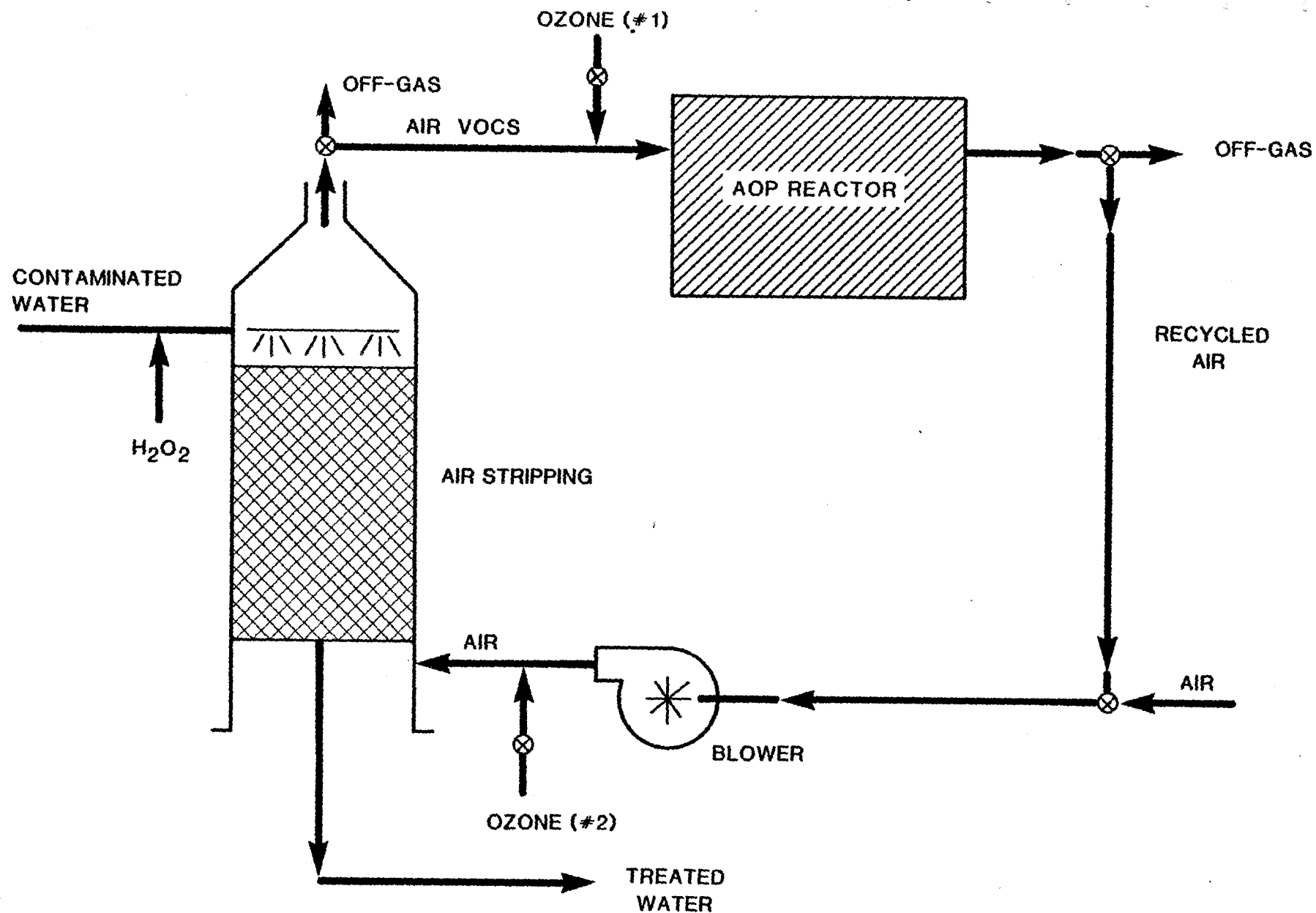
- o The spent carbon will be considered a hazardous waste and have to be hauled off site by a licensed carrier for disposal or regeneration.
- o The air stripping tower may be considered aesthetically unpleasant to local residents.

#### **AIR STRIPPING PLUS GAS-PHASE AOP**

A schematic of this treatment scenario is provided in Figure 16. Under this treatment scenario, the VOCs are stripped from the contaminated water as it flows through the stripping tower. Air stripping will effectively remove all VOCs, to 2  $\mu\text{g/L}$  or less, from the water. The exhaust gas then passes through a AOP oxidation chamber where the VOCs are destroyed. After passing through the AOP-APC system, the air can be recycled back through the packed tower.

The AOP oxidation chamber contains several UV bulbs. Photolysis of the air stream, as it passes through the chamber, generates ozone. As the ozone decomposes, hydroxyl radicals are formed. If the ozone dose generated in the reaction vessel is insufficient to effectively degrade the VOCs, ozone can be produced with an ozone generator and fed into the exhaust gas stream before it enters the UV chamber.





AIR STRIPPING WITH AOP-AIR POLLUTION CONTROL  
FIGURE 16

Several advantages of this treatment scenario are:

- o NO OFF-GAS EMISSIONS.

Theoretically, after passing through the AOP reaction chamber, the air can be recycled back through the stripping tower so that there are essentially no gas emissions. This concept has not been tested.

- o NO HAZARDOUS MATERIAL.

The VOCs will be oxidized to carbon dioxide, chloride, and water rather than simply being transferred to another medium such as activated carbon. This statement, however, assumes complete oxidation of the VOCs. If the VOCs are not oxidized in the AOP-APC chamber, they will be recycled (with the recycled gas flow) back through the stripping tower and AOP-APC system.

- o THEORETICALLY MORE EFFICIENT THAN LIQUID-PHASE AOP

Air-phase AOP oxidation, theoretically, should destroy the VOCs more efficiently (i.e., require lower UV and ozone doses) than liquid-phase AOP oxidation. This is because there are no carbonate/bicarbonate ions present in the gas phase to scavenge the hydroxyl radicals. Results from the pilot study indicate that approximately 95% of the hydroxyl radicals produced are consumed by compounds other than the VOCs. Carbonate/bicarbonate ions are generally the most prevalent hydroxyl radical scavengers.

- o OFF-GAS CAN BE ROUTED THROUGH A TEMPORARY GAC-APC RATHER THAN THE AOP-APC SYSTEM, IF EVER NECESSARY.

If the AOP-APC system ever needs to be temporarily taken out of service, the air emissions from the stripping tower can be routed through a temporary GAC-APC system. In this way, the wells can continue to be pumped and the water treated, even if the AOP-APC system is down for repairs.

- o PUBLIC ACCEPTANCE.

Because there are no off-gas emissions and no hazardous materials to dispose of, the AS+AOP-APC treatment scenario should be acceptable to the public.

The disadvantages associated with this system are:

- o THE AOP-APC SYSTEM HAS RECEIVED ONLY LIMITED PILOT-SCALE TESTING.

The AOP-APC system is a new, but promising, technology which has received only limited pilot-scale testing. Results from this testing, however, indicate that it can be used effectively to destroy TCE and PCE. Because of minimal testing, the effectiveness, system size, optimum UV dose, optimum ozone dose, and cost of a full-scale AS+AOP-APC facility is not known. For cost estimation purposes, assumptions were made about the required UV dose, ozone dose, etc.

- o THE AOP-APC SYSTEM HAS NEVER BEEN TESTED FOR CTC REMOVAL.

The limited pilot-scale testing of the AOP-APC system did not include CTC oxidation. Of the three VOCs of concern (i.e., TCE, PCE, and CTC), only TCE and PCE oxidation have been tried. However, the percent removals seen for both of these compounds was good (TCE  $\cong$  90% removal, PCE  $\cong$  80% removal).

- o CAPITAL AND O&M COSTS UNCERTAIN.

Because AOP-APC is a new technology and the system has never been pilot tested with the intent of designing and building a full-scale facility, there is a great deal of uncertainty associated with an estimated cost of a full-scale AOP-APC system. The costs of designing, building, and operating an air stripping tower are well established. However, a pilot-scale evaluation of the process would be required in order to obtain the information needed to estimate the cost of an AOP-APC system (e.g., UV dose, Ozone dose, contact time, etc.). The cost estimates for AS+AOP-APC, included in the report, were based on several "best guess" assumptions about operational requirements.

- o TALL STRIPPING TOWER IN RESIDENTIAL AREA.

Stripping towers are generally tall and may be aesthetically displeasing to local residents. However, they can be modified architecturally so that they blend in with their surrounding and are less offensive to area residents.

- o PROCESS NOT EFFECTIVE AT REMOVING NON-VOLATILE POLLUTANTS FROM WATER.

Air stripping will not remove non-volatile pollutants from water. Should contamination by non-volatile toxicants become a problem in the future, an alternative treatment process would have to be employed.

- o Since the VOCs are destroyed rather than being transferred from one medium to another, there are no hazardous materials to dispose of and no VOCs emitted to the atmosphere.

- o Air-phase AOP oxidation should be much more effective than liquid-phase AOP because there are no carbonate/bicarbonate ions present in the gas phase to scavenge the hydroxyl radicals. Results from the ULTROX/WMI pilot study indicate that, in the case of Pasadena's water, approximately 95% of the hydroxyl radicals produced are consumed by compounds other than the VOCs. Carbonate/bicarbonate ions are generally the most prevalent hydroxyl radical scavengers.

The primary disadvantage of this system is that it is a new technology and has only been tested twice--once by JMM and once by a consulting engineering firm in the Netherlands-- at the pilot scale (without an external ozone source). The one AOP-APC pilot test performed by JMM evaluated the removal of TCE and PCE from the exhaust gas of an air stripper. The results indicated good removals for all of these compounds (TCE  $\cong$  90%;

PCE  $\cong$  80). However, the system was not tested for CTC removal. The AOP-APC system was also tested, in conjunction with an air stripper, during a pilot study performed in the Netherlands (McGregor, et al., 1987). In that study, it was used to treat a groundwater contaminated with TCE, PCE, and chloroform. Results from this study indicated total VOC removals of greater than 99%. Again, however, the system was not tested for CTC removal.

## **ESTIMATED COST FOR FULL-SCALE TREATMENT**

Cost estimates were prepared for design, construction, and operation of each of these alternative treatments. Since the AOP parts of these scenarios are extremely new technology, the accuracy of the estimates cannot be guaranteed to be within the usual range for feasibility level estimates-- -30% to +50%. However, they do provide a good indication of the cost of each scenario relative to the costs of the Ultrox UV/ozone process evaluated in the Treatability/Feasibility report, and  $H_2O_2$ /ozone by itself. The assumptions and design criteria used for these estimates are shown in Table 13 and the cost estimates are compared in Table 14. When reviewing these costs estimates, it should be stressed that very little is known about the design of an AOP-APC system; thus, for this process, the design criteria were assumed (based on JMM's experience with the AOPs) rather than known. The accuracy of the cost estimate for each viable alternative is given in Table 15.

As indicated, three of the eight listed treatment alternatives are not viable methods for removing TCE, PCE, and CTC -- air stripping alone, liquid-phase UV/ozone, and liquid phase  $H_2O_2$ /ozone. The reasons they are not viable are included in Table 14. In regard to economics, the cost of implementing the various viable treatment scenarios increase in the following order:

AS + AOP-APC

AS + GAC-APC

$H_2O_2$ /Ozone + AS + GAC-APC

$H_2O_2$ /Ozone + GAC

GAC alone

When reviewing these costs, it should be pointed out and stressed that, for any alternative processes using activated carbon, the O&M costs may be underestimated. All cost

TABLE 13

**ASSUMPTIONS AND DESIGN CRITERIA USED FOR ESTIMATING  
THE COSTS FOR THE ALTERNATIVE TREATMENT SCENARIOS**

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**General**

Flow Rate	=	4155 GPM
Pump Usage	=	67%
Amortization Period	=	20 years
Interest Rate*	=	8%
Power Cost*	=	\$ 0.074/KWH

**H<sub>2</sub>O<sub>2</sub>/Ozone + GAC**

Effectiveness of H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> :	TCE	=	99%
	CTC	=	50%
	PCE	=	75%

**H<sub>2</sub>O<sub>2</sub>/Ozone + Air Stripping  
+ GAC Air Pollution Control**

Effectiveness of H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> :	TCE	=	99%
	CTC	=	50%
	PCE	=	75%

**Air Stripping + AOP Air\*\*  
Pollution Control**

Ozone Dose	=	3 mg/L (of water)
UV Dose	=	75 watt-sec/L (water)
UV wavelength produced by bulbs	=	254 nm
UV bulb life	=	8000 hrs
Cost of ozone generation	=	10 KWH/lb O <sub>3</sub>

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\* Information supplied by the City of Pasadena.

\*\* The capital cost was assumed to be the same as AS + GAC-APC.

TABLE 14

COMPARISON OF ESTIMATED TREATMENT COSTS FOR  
ALL ALTERNATIVE TREATMENT PROCESSES CONSIDERED

Treatment Alternative	Viable Alternative	Reason If Not Viable	Total Capital Cost (\$)	Annual O&M Cost (\$/Yr)	Total Annual Cost (\$/Yr)	Unit Cost (\$/AF)
Air Stripping	No	AQMD will not approve the use of this process without APC if > 11b/day of VOCs are discharged. (Regulations pending.)	\$ 550,000	\$ 44,000	\$ 100,000	22
H <sub>2</sub> O <sub>2</sub> /Ozone	No	Does not effectively remove CTC.	387,000	81,000	121,000	27
Air Stripping plus AOP Air Pollution Control	Yes (?)	This is a new technology; not sure if it will effectively remove CTC.	1,890,000	130,000	323,000	72
Air Stripping and GAC Air Pollution Control	Yes		1,200,000	340,000	460,000	104
H <sub>2</sub> O <sub>2</sub> /Ozone plus Air Stripping plus GAC Air Pollution Control	Yes		1,600,000	300,000	470,000	105
H <sub>2</sub> O <sub>2</sub> /Ozone plus GAC	Yes		2,300,000	300,000	540,000	120
Granular Activated Carbon (GAC)	Yes		1,950,000	380,000	580,000	130
UV/Ozone (Ultrox, revised)	No	Does not effectively remove CTC.	3,822,000	581,000 (462,000)	970,000 (851,000)	216 (190)

\* The numbers in parentheses were based on an ozone power consumption of 10 KWH/lb O<sub>3</sub> which is the industrial average. The other numbers were based on a power consumption of 18.8 KWH/lb O<sub>3</sub>, determined during the pilot study.

**Table 15****Accuracy of Cost Estimates  
for Viable Alternatives**

Treatment	Accuracy
AS + AOP-APC	-40% / +140%
AS + GAC-APC	-30% / +50%
H <sub>2</sub> O <sub>2</sub> /Ozone + AS + GAC-APC	-30% / +60%
H <sub>2</sub> O <sub>2</sub> /Ozone + liquid-phase GAC	-30% / +60%
GAC alone	-30% / +50%

estimates (including those in the Treatability/Feasibility report) assumed a maximum TCE concentration of 200  $\mu\text{g/L}$  and a maximum CTC concentration of 50  $\mu\text{g/L}$ . This estimate used for CTC may in fact be too low; current CTC concentrations at Well #25 are about 20  $\mu\text{g/L}$ . Since the carbon has a lower capacity for CTC than it does for TCE or PCE, the carbon usage rate is primarily dependent on the CTC concentration. If the CTC concentrations in the aquifer exceed 50  $\mu\text{g/L}$ , O&M cost for carbon replacement will also increase proportionally.



**SECTION 7**

## SECTION 7

### CONCLUSIONS

Based on the results of this UV/ozone pilot study, the following conclusions can be made:

- o The WMI UV/Ozone system demonstrated the following VOC removals:

TCE = 50% removal

PCE = 50% removal

CTC = 15% removal.

Thus, this treatment system is not capable of providing satisfactory treatment for the City's VOC contaminated groundwater.

- o The ULTROX UV/Ozone system demonstrated the following (maximum) VOC removals:

TCE = 99% removal

PCE = 99% removal

CTC = 80% removal.

Under the optimum operating conditions for TCE and PCE removal, only 50% - 60% CTC removal is attained. Thus, the ULTROX system can provide effective treatment for TCE and PCE, but not for CTC.

- o H<sub>2</sub>O<sub>2</sub>/ozone oxidation can provide a degree of treatment comparable to UV/ozone oxidation, but requires a much lower ozone dose and shorter contact time. Based on limited testing, H<sub>2</sub>O<sub>2</sub>/ozone does not provide satisfactory removals of CTC.
- o Of all the treatment processes considered, the only viable alternatives are:

Air Stripping plus AOP-APC

Air Stripping + GAC-APC

H<sub>2</sub>O<sub>2</sub>/Ozone + Air Stripping + GAC-APC

H<sub>2</sub>O<sub>2</sub>/Ozone + GAC

GAC

The first alternative--Air Stripping plus AOP-APC, is known to be effective in destroying TCE and PCE, but has never been tested for CTC removal. This treatment scenario, however, is the only one that would actually destroy the VOCs rather than simply transferring them to the GAC for subsequent regeneration or disposal.

- o Of the viable treatment alternatives, their estimated costs increase in the following order:

Air Stripping plus AOP-APC

Air Stripping + GAC-APC

H<sub>2</sub>O<sub>2</sub>/Ozone + Air Stripping + GAC-APC

H<sub>2</sub>O<sub>2</sub>/Ozone + GAC

GAC

## TREATMENT OPTIONS

As a result of the difficulty experienced in oxidizing CTC when it is in water. UV/Ozone oxidation is no longer considered a viable alternative for treating the City's contaminated well water. Peroxide/Ozone oxidation also is not effective at removing CTC from drinking water. Thus, the treatment options available to the City are:

1. Proceed with the design and construction of liquid phase GAC treatment which is known to be effective in removing TCE, PCE, and CTC from drinking water. Use of GAC adsorption has the following advantages and disadvantages:

### Advantages:

- It has been shown to remove greater than 99% of TCE, PCE, and CTC.
- If used for liquid phase adsorption, it can also be used to remove many nonvolatile contaminants from the water.

### Disadvantages:

- The spent carbon must be transported off site for proper disposal or regeneration.

- If the VOC concentrations in the contaminated well water increase to higher than projected levels, the carbon usage rate and associated O&M costs will increase proportionally. This is of particular concern for CTC since (1) its current concentration is already about half of the concentration used for estimating treatment costs and (2) GAC has a lower capacity for CTC than it does for TCE and PCE.
- Highest cost of all viable alternatives.

## 2. Construct a full-scale air stripping tower plus GAC-APC system.

The advantages are as follows:

- This is a proven technology for the removal of VOCs.
- Cost for air stripping plus GAC-APC is lower than cost for liquid phase GAC

Disadvantages include:

- The spent carbon will require proper disposal or regeneration.
- Disadvantages associated with air stripping towers, aesthetic appearance and noise.
- Cost of this system is dependent on the changes in concentrations of VOCs. Usage rate of GAC and associated O&M costs will increase with increase in VOC concentrations. Increase in concentration of CTC is of particular concern, since GAC has a lower capacity for CTC than it does for TCE and PCE.
- Air stripping will not be effective for non-volatile compounds.

## 3. Perform a thorough pilot test evaluation of the air stripping plus AOP-APC process prior to deciding which of the viable treatment alternatives would provide the best full-scale treatment. Details of the extended pilot-scale evaluation will be given later in this section. If the AOP-APC system is proven effective in the pilot study, the following advantages and disadvantages should be considered:

#### Advantages:

- The VOCs are (presumably) oxidized to carbon dioxide and water rather than being transferred to another medium.
- After passing through the AOP reaction chamber, the air can, theoretically, be recycled back through the stripping tower so that there are essentially no gas emissions. This concept, however, has not been tried.
- If the cost estimates are correct, it is the least expensive of the viable treatment alternatives.

#### Disadvantages:

- All the disadvantages associated with the use of an air stripper including its ineffectiveness for non-volatile compounds.
  - The AOP-APC system is a new technology and needs to be piloted before it can be guaranteed to effectively remove all three VOCs of concern. The system has been tested for TCE and PCE removal, but never for CTC removal
  - There will be a time delay imposed by another pilot study prior to design for full-scale treatment. This delay could result in spreading of the contaminated plume to other wells, which could mean further costs to purchase replacement water or treatment systems.
4. Begin the thorough pilot-scale study of the air stripping plus AOP-APC treatment system, and simultaneously, design the full-scale air stripping portion of the treatment facility. The decision to design for full-scale AOP emissions control, or full-scale GAC emissions control, could be made near the end of the extended pilot study. This will minimize the time delay in construction of a full-scale treatment system, since the air stripper is a common element to both emissions control options. Minimizing this time delay would minimize further problems and costs associated with the spread of the contaminated plume to other wells.

Advantages and disadvantages of the AS + AOP-APC and AS + GAC-APC options have already been discussed above.

JMM recommends that option 4 be selected since it is the most environmentally sound and economical of the viable alternatives, which will accomplish the treatment objectives in a timely fashion. This option will allow for the most cost effective air stripper with emissions control system with the minimum time delay. The AS + AOP-APC process is the only viable alternative that has the potential to completely destroy the VOCs rather than simply transferring them to another medium. However, the AOP-APC system is a conceptual technology and should be piloted before being recommended for full-scale implementation. Under option 4, a complete treatment system utilizing either GAC or AOP for emissions control, would be completed and operational within 23 months.

The work proposed for the independent pilot study is described in the following paragraphs.

#### **Extended Pilot-Scale Evaluation**

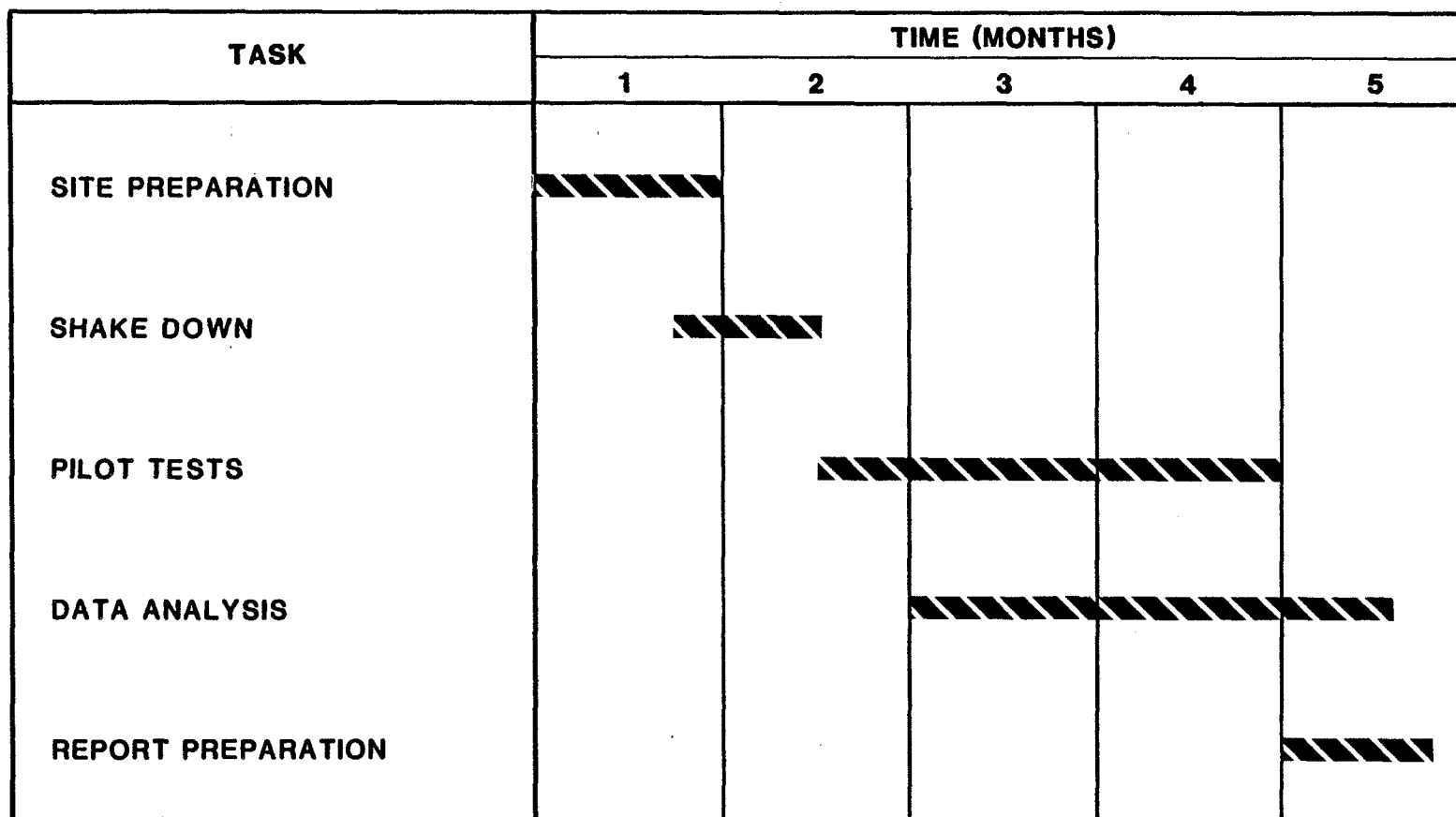
A schematic of the pilot AS + AOP-APC treatment system was shown in Figure 16. A side stream of water from Windsor Reservoir will be spiked with the three TCE, PCE, and CTC and piped to the top of the stripping tower. The contaminated water will flow downward through the packing to the bottom of the tower. At the same time, air is forced upward from the bottom of the tower, counter-current to the direction of the water flow. While the air and water are in contact with each other, the VOCs are stripped from the water and transferred to the air where they are exhausted out the top of the tower. Instead of being discharged directly to the atmosphere, the exhaust air (now contaminated with VOCs) will pass through the AOP-APC chamber where the VOCs are oxidized to carbon dioxide and water. (The amount of water generated, most likely, will not be enough to actually condense and form water droplets.) Attempts will be made to recycle the treated off-gas back through the stripping tower.

The AOP-APC chamber will contain several UV lights. As the air from the stripping tower passes through this system, it will be irradiated and ozone will be formed. Auto-catalytic decomposition of ozone will result in the formation of hydroxyl radicals. If the amount of ozone (and thus hydroxyl radicals) in the AOP reactor is insufficient to

effectively degrade the CTC, ozone can be generated externally (using an ozone generator) and fed into the air stream just before it enters the AOP reactor.

Reducing the VOC load entering the AOP-APC system may improve the overall effectiveness of the treatment process. This can be accomplished by employing AOP treatment of the liquid-phase in addition to AOP treatment of the gas-phase. Under this scenario, peroxide will be spiked into the contaminated water before it enters the stripping tower and ozone will be fed into the air stream (ozone feed point #2) entering the bottom of the tower. Thus, liquid-phase  $H_2O_2$ /ozone oxidation will be taking place in the tower at the same time the VOCs are being stripped from the water.

The schedule proposed for this pilot work is provided in Figure 17.



SCHEDULE FOR EXTENDED PILOT STUDIES  
FIGURE 17



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